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Volume 17 AUGUST, 1947 Number 2

Journal of Sedimentary Petrology

A Publication of the Society of Economic Paleontologists and Mineralogists
a Division of
The American Association of Petroleum Geologists

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Articles submitted for publication to the *Journal of Sedimentary Petrology* should have a prefatory abstract and sufficient postage should be sent by the author to pay the return of the manuscript as it has been found that many articles require more or less revision before publication.

Persons who are not members of the Society of Economic Paleontologists and Mineralogists or are not subscribers to the *Journal of Sedimentary Petrology* but who desire to publish an article in the *Journal*, should have some member of the Society of Economic Paleontologists and Mineralogists or some member of the American Association of Petroleum Geologists sponsor the article. Members of these Societies are given preference in publication.

JOURNAL OF SEDIMENTARY PETROLOGY, VOL. 17, NO. 2, PP. 39-67
PLATES I–IV, FIGS. 1-5, AUGUST, 1947

PISOLITHS AND OOLITHS FROM SOME AUSTRALIAN CAVES AND MINES

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Victoria, Australia

ABSTRACT

The occurrence, nature and origin of calcareous concretions, principally of the pisolithic type, developed in pools on the floors of caves and mines in Australia, are described from (i) a cave near Cape Schanck lighthouse on the south coast of the Mornington Peninsula, south central Victoria; (ii) the Murrendal Caves near Buchan in Eastern Victoria; (iii) a cave at Chillagoe, Queensland; and from mines at (a) Bendigo in the Northern district of Victoria, (b) St. Arnaud in the Wimmera district of Victoria, (c) Harrietville in the northeastern district of Victoria and (d) Broken Hill in New South Wales. Pisoliths are also recorded from (e) the Ballarat mining district in Victoria.

INTRODUCTION

Discrete concretions of calcite in caves and mines are mainly pisoliths and occasionally ooliths. They have been referred to as "pellets," as "small rounded balls" and, where well polished, as "cave pearls." They mostly occur free in shallow pools situated either on ledges or on the floors of caves and drives in mines; sometimes they become cemented to the calcareous encrustations on these floors. Few occurrences have so far been described from other parts of the world, and up till now, none from Australia has been studied in detail.

In other countries, the concretions have been noted in approximately twice as many mines as caves. E. Erdman (1902) recorded them from a mine in Sweden, R. C. Emmons (1928) from the Hidden Fortune Mine at Lead, South Dakota. S. C. Davidson and H. E. McKinstry (1931) recorded pisoliths from two mines at San Dimas, Durango and one at San Francisco de Yoquivo, Chihuahua, all in Mexico. J. H. Mackin and H. A. Coombs (1945) found examples of pisoliths in a mine in the Iron Mountain district of south-western Idaho.

Pisoliths are known from the Carlsbad Caverns in New Mexico (W. T. Lee, 1925 and F. L. Hess, 1929), from a cave in Missouri (W. D. Keller, 1937), from the "Cave of Mounds," U.S.A. (A. W. Pond, 1945) and from the "Grotte de Cagire" in the Pyrenees, France (N. Casteret, 1939).

To this list now has to be added ocurrences from five mining districts and three caves in Australia.

Comparable discrete concretions in the form of ooliths, developed in the coil of a water-heating system, have been described by W. H. Twenhofel (1928), and in the form of pisoliths (of unique occurrence) in a mineral spring (Jemez Springs) in New Mexico, described by S. A. Northrop (1934).

The rarity of pisoliths and ooliths in caves is stressed by Casteret (1939, foreword). His examination of 500 caverns and underground watercourses revealed pisoliths in only one cavern. Evidently the special conditions requisite for the the natural formation of pisoliths and ooliths in caves are infrequently attained.

AUSTRALIAN OCCURRENCES OF PISOLITHS AND OOLITHS

Section A. Cave Pisoliths

Angel Cave, Victoria

This cave is dealt with in rather greater detail than the other Australian occurrences, since a considerable number of observations have been made therein. The cave is situated in the Cape Schanck area of the Mornington Peninsula, 52 miles south of Melbourne (fig. 1).

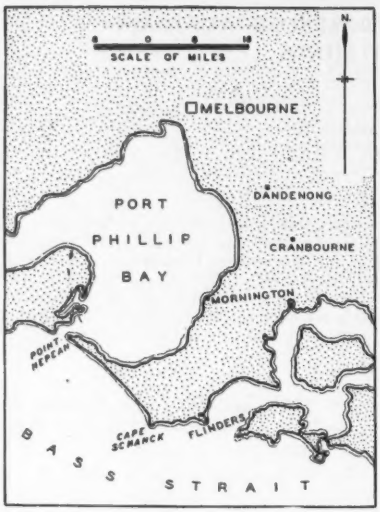

FIG. 1.—General Locality Map showing the position of Cape Schanck.

The cave has been cut in Older Tertiary basaltic lava and tuff at the head of a small bay trending southwest, near Cape Schanck lighthouse in the Parish of Fingal, County Mornington (fig. 2).

Cemented and partially consolidated Quaternary dune limestone overlies the basalt in this area.

Nature of Angel Cave

The cave, which extends for approximately 100 feet into the base of a high cliff of basalt, has a gradually rising floor for the first 50 feet, at which point it is about 5 feet higher than the entrance. Thereafter, it rises more abruptly until the back of the cave is some 20 feet higher than its entrance.

The cave entrance consists of an outer and an inner portal. The outer opening, 14 feet wide, is surmounted by a series of pendant carbonate growths. Ten feet beyond, similar pendants narrow the inner portal to 8 feet in width and 5 feet in height. Beyond the inner portal, the cave increases in size until some 40 feet in from the sea cliffs, it is 30 feet wide and 30 feet high (fig. 3).

The roof and wall of the cave northwest of the inner portal are liberally ornamented with clusters of short, narrow, tubular stalactites averaging 5 cms. long and 5 to 7 mm. in diameter. About half way up the wall, just beyond the inner portal, a much larger stalactite and stalagmite have united to form a column. With subsequent outgrowths, this has developed into a structure said to simulate, under certain conditions of lighting, the figure of an angel with folded wings, hence the name "Angel Cave," applied by the local inhabitants.

Little calcareous matter occurs on the southeast wall of the cave, although a few small stalactites hang from the roof nearby. Most of these are dry, but occasional drops of water fall from adjacent joints in the roof. By far the most sustained dripping of water occurs on the opposite (northwest) side of the cave, more particularly above a ledge which runs along part of the wall (see fig. 3). The ledge and the greater part of the cave floor beneath, are thickly covered with a calcareous encrustation, lacking only in the tunnel-like rear portion of the cave. This encrustation is of uneven thickness; at one point, it was chipped away to a depth of 1½ inches without being completely penetrated, and here it showed many banded layers.

Cementation by $CaCO_3$ of beach-worn boulders (up to 2 feet by 2 feet 6 inches) at the cave entrance beneath the pendant growths (fig. 3), has formed a step approximately 18 inches above the height of the steep cobble beach which lies outside the cave. This feature is important in forming a barrier to normal high tide erosion. The lower reaches of the cave floor also consist of cemented boulders, cobbles and pebbles; the spaces between these have been almost filled with secondary carbonate. Generally, however, the surface of the cave floor has not been uniformly smoothed by accretion of calcium carbonate. Small, regular pools and larger irregular basins are in evidence along the

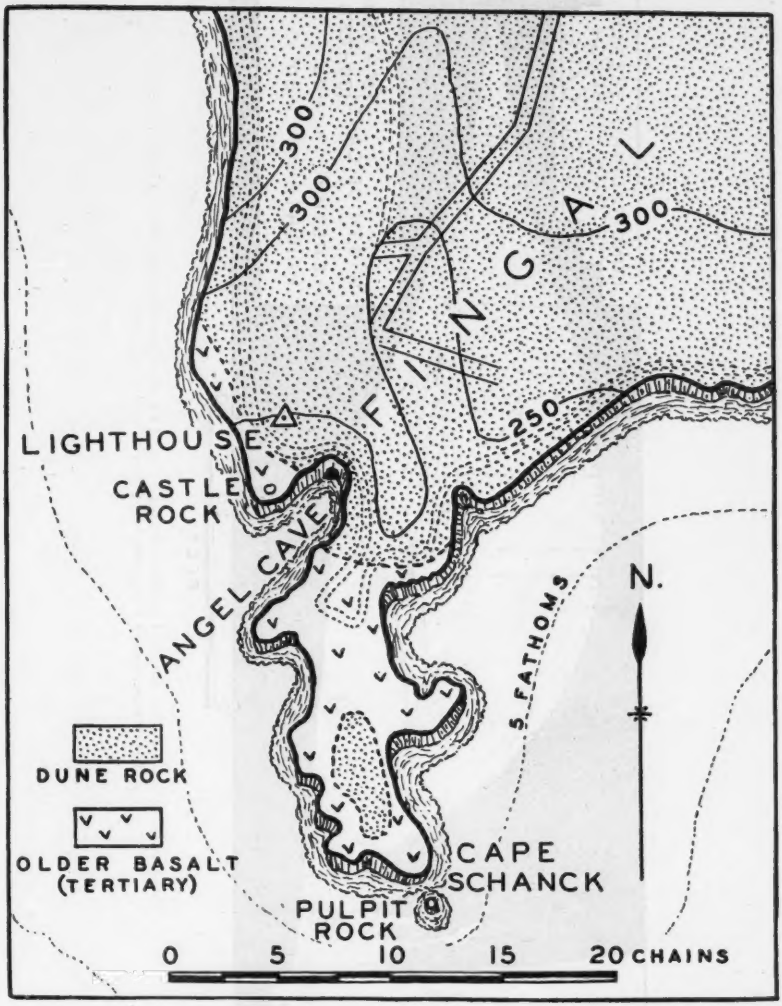

FIG. 2.—Detailed Locality Map, showing the position of Angel Cave. (Based on an unpublished plan, prepared by R. A. Keble, at the Victorian Mines Department.)

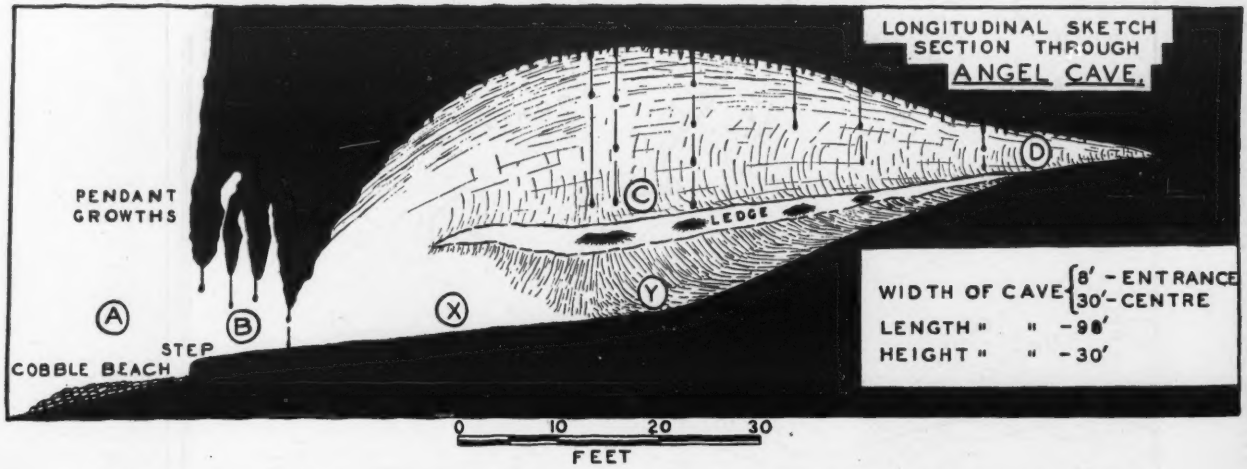

FIG. 3.—Diagrammatic Longitudinal Section (N.E.-S.W.) through Angel Cave, Cape Schanck. A, B, C and D = points where temperatures were measured. For X and Y see text.

northwest margin of the more gently sloping portion of the floor, between B and Y in fig. 3, also near the middle of the more abrupt slope extending from Y to D in fig. 3, and on the ledge (fig. 3). A few pools occur at the back of the cave, where the encrustation on the floor is not so well developed.

The groups of pools along the ledge are of especial interest, because many of them contain a large number of the discrete calcareous concretions, pisoliths and ooliths, forming the principal subject matter of this paper. A few dozen of these pools occur in the cave. They vary in size from 2 inches to 2 feet or so across, and ¼ inch to 4 inches deep; they contain from as few as 3 to as many as 2,000 and more pisoliths and ooliths. In pools full of pisoliths and ooliths, the larger ones (around 20 mm. long) occur at the top, flush with the edge of the pool, the smaller ones (down to 1 mm.) occur at the bottom of the pool. It is not known how many pisoliths and ooliths have been generated in any particular pool, because the top ones in overcrowded pools become pushed out with continued growths, and some may even be washed out by higher seas that occasionally enter these parts of the cave.

No obvious retaining rims are developed around pisolith-bearing pools. In fact, rim-growth is probably inhibited by the fact that the floor around the pools is continually wet from splash, from overflow of the pools and from seepage generally down the walls and across parts of the cave floor. Such conditions would tend to produce more or less even deposition on the calcareous crust around the pools. The walls and floors of the pools containing pisoliths have smooth surfaces, some of them partially, others well-polished.

Origin of Angel Cave

As early as 1864, Harrison had regarded Angel Cave as resulting from—"a soft stratum of basalt . . . being eaten away by successive tempests and the percolation of land springs." Field observations point to this cave having been formed by selective marine erosion along a four-feet thick layer of soft, red, tuffaceous material; this is interbedded with the basalt flows that form the cliffs below Cape Schanck lighthouse (fig. 2). The tuffaceous material is exposed in the cave, being unobscured by calcareous encrustations for a short distance at the back of the cave, and it forms part of the northwest wall. Underground waters percolate along the junction of this layer with the overlying basalt flow. Much smaller caves have been formed in this tuffaceous layer in the cliffs west of the entrance to Angel Cave; they are subject to wave action at normal high tide.

Features of the Floor of Angel Cave

Under calm marine conditions, Angel Cave is protected from wave action by the steep cobble beach outside, as well as by the step, 18 inches higher at the cave mouth (fig. 3). On rare occasions, however, beach material is carried into the cave for some distance, and under severe storm conditions, no portion of the cave is immune from at least a little wave action. In 1937, the cave floor was relatively free of rock débris, but in 1943 and 1946, basaltic shingle was strewn about on the southeastern side for up to 32 feet from the entrance (near X in fig. 3). Several pebbles, cobbles and boulders had been transported to the foot of the rise (at Y in fig. 3), some 50 feet from the entrance, and there firmly cemented to the cave floor. The largest boulder near the inner portal was 1 foot across, and like others in the vicinity, was not cemented to the cave floor.

In 1945, water-worn pebbles of basalt, averaging 2 to 3 inches in length, were observed in pools at the rear of the cave, about 98 feet from the entrance. One, weighing 2 pounds (Plate IV, fig. G), and several others had rested sufficiently long in a pool on the ledge (fig. 3) to have become partially encrusted with calcium carbonate. Moreover, many of the pisoliths in pools seemingly remote from wave action, possess nuclei of basalt

fragments. In addition, a few recent marine shells, now encrusted with secondary $CaCO_3$ (Plate IV, fig. C) have been found in some of the pools, likewise the appendages and carapaces of crabs (also encrusted). It is thus apparent that that waves occasionally traverse the whole length of the cave, carrying in beach-worn boulders, cobbles, pebbles, shingle and the remains of marine organisms. Usually, only the lower reaches are disturbed by marine incursions, although some material is occasionally carried to positions between these limits, and allowed to remain there in a static position long enough for cementation to occur.

The entry of the sea from time to time, must temporarily disturb the conditions favorable to pisolith and oolith formation in the pools on the cave floor. Some pools may thereby have their contents of discrete calcareous concretions swept away, and the carbonate water diluted or completely replaced by sea water. This, however, is only a transient phenomenon, and when the high seas abate, conditions on the cave floor soon return to those prevalent before marine incursion, and the accretion of pisoliths and ooliths is renewed. It is probable that under such conditions, pisoliths generated in one pool (perhaps fed by fast-dripping feeders), may be swept by wave action into a pool subject to different conditions (perhaps fed by slow-dripping feeders or seepage waters). If left long enough in the new pool, the pisoliths would continue to grow in their new environment, and thus change in character. Evidence to support this suggestion is found in a pool generating principally very rough-coated pisoliths; smoother bisque-surface types are also found in small numbers in the same pool, some partially encrusted.

Pebbles of basalt brought in by the sea and lodged in pools in the cave do not become cemented to the floors of the pools. On the contrary, they remain free and provide some indication of the conditions controlling carbonate precipitation in Angel Cave. Deposition of $CaCO_3$ reaches its maximum at the surface of the water in each pool, as indicated by the occurrence of a partially immersed basalt pebble with a "plimsol-line" (Plate IV, fig. G). The "plimsol-line" is represented by thin, but well-developed bands of calcium carbonate encircling the projecting pebble at the level to which it was immersed in the calcareous waters of the pool; carbonate deposition dwindles to a minimum near the point of contact of the pebble with the floor of the pool. In contrast to this, pebbles left stranded on the stalagmitic crust on the cave floor, and likewise pisoliths which have rolled out of overcrowded pools and now rest on a sloping (and therefore well-drained) surface, commonly become cemented in place. Additional evidence showing that maximum $CaCO_3$ deposition occurs at the surfaces of pools, is provided by eave-like growths of carbonate layers out from the sides of nearly stagnant pools, thus forming small ledges, a few millimetres thick, just at water level.

Origin and Nature of the Carbonated Waters in Angel Cave

It is improbable that the mineral matter carried in solution by vadose waters issuing in Angel Cave, was derived entirely from the decomposition of the basalts in this district. The basalts contain only 10% of CaO (Edwards, 1939, p. 90), and since the rock is relatively fresh it would have yielded but minor amounts of the lime required. A more probable source lies in the dune limestone overlying the basalt. A sample of this rock outcropping near a track up the cliff southeast of Angel Cave, was found to be 53.5% acid (HCL) soluble. The sample was somewhat friable, and may have have been partially leached, as the $CaCO_3$ content of other Victorian dune limestones is known to be much higher, up to 98.75% in some (Coulson, 1940, p. 330).

The conclusion is that the carbonate waters derived from the dune limestone, percolate downwards along joint planes

in the basalt and along planes of separation between lava flows and inter-bedded tuffaceous bands. Some of these waters issue in Angel Cave, where conditions are suitable for the gradual growth of such secondary carbonate formations as stalagtites, stalagmites, calcareous encrustations, pisoliths and ooliths.

Melhuish and Deane (1937), referring to Angel Cave as "Cave B" at Cape Schanck, recorded the water in the pools on the floor of the cave as being of "mineral character only," i.e., the pool waters contained no living organisms, so that the contained pisoliths and ooliths have not been precipitated by organic processes.

Two samples of the cave waters were analysed in the State Laboratories by Mr. F. F. Field, and showed the proportions of carbonates and bicarbonates set out in Table 1.

TABLE 1

	I.	II.
Carbonates (CO_3) in parts per 100,000	nil.	nil.
Bicarbonates (HCO_3) in parts per 100,000	39.5	36.5
Air Temperature	62°F	63°F
Pool Temperature	58°F	61°F
Rate of Supply	80 cc./min.	17 cc./min.

I—collected under a fast drip (too fast to count). Cave roof near northwest wall, above middle of ledge (see fig. 3).

II—collected under a slower drip (rate of drip=116 drops a minute). Calcareous pendant on northwest side of inner portal (see fig. 3).

Assessing the amount of bicarbonate in terms of equivalent quantities of $CaCO_3$, the fast drip (Table 1, column I) gives about 32.38 parts per 100,000 and the slower drip (Table 1, column II) about 29.93 parts. Assuming the partial pressure of CO_2 within the cave to equal its present atmospheric value of 0.0003, the tables of Johnston and Williamson (1916) indicate that the solubility of calcite at 16.5°C (= temperature of cave air = 62°F) is 63.5 parts of $CaCO_3$ per 100,000. The concentration of the fast drip is therefore 50.05% and that of the slow drip 47.66%. The lower concentration of the slow drip is to be ascribed to its location near the mouth of the cave. Here, better evaporation conditions exist, so that more $CaCO_3$ is used in building stalactites. The waters dripping from stalactites under these conditions would tend to be rather less concentrated.

Since the cave waters are precipitating calcite, they are apparently slightly acidic, because Johnston, Merwin and Williamson (1916) have shown that with a higher HCO_3 content, calcite appears more readily, and that any free alkali (OH) present will, by diminishing HCO_3, be prejudicial to calcite formation and promote the appearance of the less stable forms of $CaCO_3$, such as aragonite and μ-$CaCO_3$, (the μ-$CaCO_3$ occurring in pisoliths being called ktypeite by Lacroix, and giving the same color in staining tests as aragonite). The Angel Cave pisoliths gave negative color tests, and are therefore composed of calcite, as confirmed by optical tests.

Factors Controlling $CaCO_3$ Deposition in Angel Cave

The factors controlling the deposition of calcium carbonate, insofar as they concern the growth of stalagmites in caves, may be limited to a consideration of five variables. The ranges in these, as established by Allison (1923), are set out in Table 2.

According to Allison (1923, p. 123), more than one drop per second is to be regarded as a fast drip. Over 2 cubic feet per second (perceptible) is a large air circulation. Over 50 per cent is a relatively high humidity. Over 68°F is a high temperature, and over 50 per cent is a high concentration.

Applying these criteria to the dripping waters analysed and listed in Table I (and these are typical of many others in Angel Cave), the rate of drip in one example (116 drops per minute) is high, so the symbol for this is "D". In the other example (Table I, column I), the rate of drip was too fast to count, and its symbol is also "D." The relative humidity is assumed to be high, i.e. its symbol is

TABLE 2

Factor	Symbol and Upper Limit	Symbol and Lower Limit	Ratio
Drip	D. Five drops per second	d. One drop per 5 minutes	1,500:1
Air Circulation	A. 500 cu. ft. per minute	a. ½ cu. ft. per minute	1,000:1
Relative Humidity	H. 100 per cent	h. 2 per cent	50:1
Temperature	T. 90 degrees F.	t. 50 degrees F.	—
Concentration	C. 100 per cent	c. 10 per cent	10:1

"H," since on each visit to the cave, its floor always remained wet. The air in the cave is fresh, and there is little free circulation. In regard to air circulation and temperature in Angel Cave, Table 3 is instructive.

able among the factors influencing carbonate deposition in Angel Cave. In summarised form, the variable factors are symbolised thus :—

(i)—for the fast drip—D,a,H,t,C.
(ii)—for the slow drip—D,a,H,t,c.

TABLE 3

Pool and Air Temperatures in Degrees F.

	Outside Cave		Cave Entrance		Middle of Cave		Rear of Cave	
	Air	Pool	Air	Pool	Air	Pool	Air	Pool
i. April, 1943	51	51.5	—	52.5	54	54	59	58.5
ii. February, 1945	64	—	63	61	62	58	62	59

A temperature gradient in both air and pool temperatures has been established in each instance—(i) in response to a falling air temperature (i.e. from rear of cave to entrance), and (ii) to a rising air temperature. A difference of nearly 8°F (in 1943 instance) over a distance of a little under 100 feet, leads to the assumption that the air circulation within the cave is poor, and so the symbol is "a" of Allison's variables. It is improbable that external influences would cause the air temperature within the cave to be sustained at a value much above the highest listed in Table 3; the temperature is therefore considered to be low and symbolised by "t."

The concentration of the fast drip is above 50%, that of the slower drip below 50%, and in this we find the greatest variation. (The capital letters indicate high values for the variables, lower case letters indicate low values.)

Stalagmites produced in caves experiencing these sets of variables, fall into groups 11 and 12 respectively of Allison's classification (1923, p. 122). These groups (11 and 12) possess the characteristics in Table 4.

Stalagmites of classes 11 and 12 have shallow splash cups and very large, mature diameters, most probably due to poor evaporation conditions. Now stalagmites with circumferences greater than 25 metres, generally occur as stalagmitic layers, rarely having sufficient space to attain their mature circumference (Allison, 1923, p. 125). It is therefore considered that the encrustation on the floor of Angel Cave is of the same

TABLE 4

Group	Type of Cup	Shape of face	Rate of growth in cms. per year	Circumference in metres	Variables
11	Very shallow	Convex	0.0075	138.9080	D, a, H, t, C
12	Shallow	Very blunt	0.0008	138.9080	D, a, H, t, c

nature as Allison's classes 11 and 12. Usually the area covered by initial stalagmite growth is determined by the splash of drops hitting the floor. This limited area is later exceeded in the adult stage, until the evaporation surface presented by the stalagmite is sufficiently large to cope with all the solution it receives and then the stalagmite grows vertically. In Angel Cave, however, the close proximity of the drips to one another, gave rise to overlapping in the initial stage, thus inhibiting the development of individual stalagmites of mature contour. Hence, except for the "angel" column and a special instance mentioned below, a continuous stalagmitic encrustation has been formed. By virtue of its deposition on a sloping floor, this encrustation is relatively well-drained, and has the appearance of a "stalagmitic cascade."

The surface continuity of the encrustation is broken by pools of two types. Of these, the smaller, shallow, regularly rounded basins (in plan), are kept open in the stalagmitic crust by long established and still actively dripping feeders. Such pools mark the axes of "occult stalagmites," of which they represent the splash cups. The larger, irregularly-shaped pools, may represent areas from which parts of the stalagmitic crust became broken during a former marine incursion, when the crust was much thinner. The damage to the crust in such instances, was apparently too great for subsequent repair by the carbonate-supplying feeder drips, although some repair has been effected in a few pools with eave-like growths.

A special set of circumstances has resulted in the development in parts, of a few, small, well-formed stalagmites. These project above the general level of the stalagmitic encrustation, and owe their existence to two factors. First, the feeder drips, which average 2 per minute, are much slower than those already discussed. This factor is probably responsible for the small diameter of these stalagmites. Second, the stalagmites only occur at one place on the steep slope formed where the ledge (fig. 3) plunges to floor level, where, due to more efficient drainage, evaporation is somewhat accelerated. This factor also contributes to the tendency for stalagmites with lesser diameters to develop. Despite improved evaporation, the stalagmites still retain the blunt faces characteristic of slowly-growing forms, probably because of the poor supply of nourishing solutions by the slow drips. Slow dripping also probably accounts for the absence of splash cups from all of these stalagmites. The nearest approach to splash cup formation, is the production of smooth, flat patches, about 1½ inches in diameter, centred in the blunt faces of the stalagmites.

The foregoing discussion of the conditions prevalent in Angel Cave, leads to this conclusion:—the realisation of Allison's specified limiting values for the five variable factors involved in the formation of slowly-growing stalagmites of large circumference (i.e. =stalagmitic encrustations), also automatically results in the formation of the rarely developed "nests" of pisoliths and ooliths, found in certain caves and mines. It cannot be maintained that every stalagmitic encrustation formed in response to factors promoting the confluence of neighboring stalagmites, necessarily infers the achievement of such conditions. Nevertheless, the further coincidence of factors responsible for splash cup-formation (kept open in such an encrustation by active feeders) may well do so, because, whereas, on the one hand, stalagmitic encrustation development is chiefly a function of poor evaporation conditions, splash cup formation, on the other hand, is chiefly controlled by the height and rate of the feeder drips (Allison, 1923, p. 116), as well as by good evaporation. Under a combination of conditions leading to the formation of both stalagmitic encrustations and splash cups, the development of pisoliths and ooliths is to be expected.

The Pisoliths and Ooliths in Angel Cave

The pisoliths and ooliths are found as discrete calcareous concretions in shallow pools up to 4 inches deep, thus forming "nests." Only those that have been crowded out of the "nests" by continued pisolith growth, or washed out during marine incursions, occur cemented on the slopes of the stalagmitic encrustation.

Number and Size

The number of pisoliths present in any one pool, has no especial significance, because of crowding out and washing out. The number varies with the size of the pisoliths and the size of the pools. Some large pools with over 2,000 concretions, contain an assemblage of pisoliths and ooliths with considerable size ranges, while smaller pools (2″ across) may contain only 3 average size pisoliths. Following Twenhofel's (1939) limiting sizes, the concretions with diameters less than 2 mm. are classed as ooliths, while those over 2 mm. come into the category of pisoliths. The pisoliths in Angel Cave range up to 35 mm. in length, but maximum sizes are partly controlled by the size of the original nuclei around which the carbonate is precipitated. The size also depends to some extent upon the depth and nature of the water in the pools, as this factor would control the number of growth layers developed. The largest pisolith obtained from Angel Cave, was 35 mm. long, and possessed a nucleus consisting of a large fragment from a broken stalactite (see fig. 5E).

While the majority of the smaller, crowded pools showed a percentage of discrete concretions of oolithic dimensions, one large pool contained thousands of examples ranging in size from the limiting value of 2 mm., down to less than 0.05 mm., at which point they become indistinguishable from the lighter colored mineral dust that accompanies the sample. A dozen of the larger ooliths from this pool, were found on sectioning to consist of radiate crystal fibres in three to five concentric layers. Three of these had foreign nuclei, mainly small basalt fragments, each larger than the dimensions of the smaller ooliths from the same pool.

Specific Gravity

The specific gravity of the pisoliths varies from type to type in the following manner (Table 5).

TABLE 5

Type according to nature of surface	Specific Gravity
Bisque	2.47
Papillated	2.52
Rough	2.53
Smooth	2.54
Polished	2.57
Buffed	2.59

Although the pisoliths are composed of calcite (Sp. Gr. = 2.714), they have rather low specific gravity values. This is attributable to their relatively high porosity. Some examples have higher specific gravity values than others, because they have a foreign nucleus (or nuclei) of differing size and character. In general, however, it appears from the results set out in Table 5, that the smoothing and polishing of pisoliths in the pools, tend to give greater compaction and consequent lowering of porosity effects, thus leading to slightly greater specific gravity values. The porous character of the pisoliths becomes evident when preparing thin sections and polished surfaces of sliced specimens, the more porous layers tending to retain the finer grades of grinding powder in pore spaces.

Johnston, Merwin and Williamson (1916, p. 488) considered that water held in sub-microscopic interstices among the radiating fibres of calcite, would reduce the specific gravity (and the refractive index) of calcite. They concluded that the low specific gravity value (2.51) of spherulitic calcite, earlier referred to as the type "vaterite," was actually due to water enmeshed among the fibres. This fact, and the presence of numerous, small cavities observed in

some layers (Plate III, fig. A) in pisoliths, led to the determination of the specific gravity value of the Angel Cave pisoliths in the powdered state. The value obtained for a bisque-surface type with no apparent foreign nucleus, was 2.724 in the powdered state, the specific gravity of the complete form being 2.47. This indicates conclusively that low specific gravity values in the pisoliths result from their porosity, while the specific gravity of the powdered form indicates that they are composed of calcite.

Brittleness and Solubility

In the polished varieties of pisoliths (known as "cave pearls") the outer polished lamina is very brittle, and always tends to split away during thin section preparation. Pisoliths free of a foreign nucleus are completely soluble in N/20 HCl, thus indicating that clay minerals are not involved in pisolith growth in Angel Cave, even though many underground waters carry small amounts of insoluble matter in a finely divided state. If present, such material settles out in the pools as red clay. Being usually present in minute amounts, it does not interfere with carbonate precipitation in Angel Cave.

On heating the pisoliths in a closed tube, small amounts of water are evolved, the pisoliths become chalky and plainly reveal concentric and radiate internal structures. In this state, however, they crumble readily and rub to a fine, white powder.

Shape and Nature of Surface

Whereas the shapes of the ooliths are invariably spheroidal, many shape varieties occur among the pisoliths. Most pisoliths having a simple shape, are uninucleate, but some are compound forms moulded about several nuclei (Plate I, fig. D, top row) that were initially welded together during conditions approaching stagnation in crowded pools. The term "stagnation," as herein applied to conditions of pisolith growth, refers to lack of oscillation and lack of rotation of the pisoliths; it does not necessarily imply cessation of circulation of the pool waters. Where stagnant conditions do not prevail, and the pisoliths of a crowded pool are caused to oscillate, but not rotate, under the stimulus of the feeding drip, then polyhedral types (Plate I, figs. B and D) are commonly developed.

Pisoliths and Ooliths with Rough and Papillate Surfaces

Where occasional, large pisoliths rest upon a pile of much smaller individuals their upper surfaces sometimes project out of the pool, thus directly intercepting the feeder drip. Although capable of promoting oscillation, drip is not competent to cause complete rotation of these larger forms, and so the surfaces of projecting pisoliths moving over the smaller supporting pisoliths (submerged), develop a high polish, but the upper surfaces remain dull and chalky in appearance.

On the other hand, some small pisoliths in the lower parts of a crowded pool, are somewhat remote from the eddies promoting oscillation, and are fed by waters partially impoverished in carbonate. These conditions result in types with quite rough surfaces. Rough-surfaced forms (Plate I, fig. C), however, are typically developed in the large irregularly-shaped pools fed chiefly by waters seeping across the floor of the cave. The surfaces of these pools are but gently rippled by splash from nearby feeders, and the pisoliths generated within them are much larger than the average met with in crowded pools. The pisoliths from these pools are invariably rough-surfaced, they occupy only a small percentage of the total volume of the containing pool, and in but few instances were found to be growing in contact with a neighbouring pisolith.

The rough-surfaced pisoliths are clearly products of relatively stagnant conditions of $CaCO_3$ deposition. Sections through them indicate that the amount of agitation produced by the feeders, must have varied during their growth,

because among interior layers there may be as many as three main bands characteristic of smooth-coated forms, alternating with rough-coated layers (Plate III, fig. A). The smooth-surfaced layers were generated during periods of agitation, the rough-coated layers during conditions of relative stagnation. Variations in the degree of agitation of the waters in certain of the pools, is apparently due to temporary cessation, or perhaps migration, of the feeder drips, but no evidence could be adduced to indicate seasonal periodicity.

Pisoliths with Polished Surfaces

Well-rounded and highly polished pisoliths like those referred to as "cave pearls," are not common in Angel Cave. Apart from an occasional specimen found among the larger pisoliths near some pool surfaces, the best group of "cave pearls" (Plate I, fig. A) came from a small pool two years after most of its original contents had been removed.

The first collection (in April, 1943) from this pool yielded 609 pisoliths and ooliths. The largest pisolith was 26 mm. in length, and consisted of carbonate layers moulded about a large basaltic nucleus. A few rounded, polished forms also occurred, together with a number having a single, slightly concave facet. Among the smaller examples, polyhedral forms were dominant, while those of oolitic dimensions were commonly multinucleate. Occasional large, formerly rough-surfaced examples were found to be in the process of having their surface excrescences polished off, due to the motion imparted by a feeder issuing from a point 6 feet 6 inches above the pool surface, at the rate of 20 drops per minute.

At the time the second collection was made (in February, 1945) after a lapse of one year and ten months, a marked acceleration in the rate of drip was evident, the feeder being now an almost continuous stream of drops too rapid to count. The few pisoliths still occupying the pool, were observed to leap about under the action of this powerful feeder. Although most of them still had the irregular form impressed upon them during the former period of crowding, the majority had become highly polished (Plate I, fig. A), and the rest were at least half-polished over the whole of their surfaces, irrespective of shape.

This particular pool thus provides evidence of the existence and the effects of variation in rate of drip of nourishing solutions. Irregularly-shaped pisoliths may therefore become polished all over, if free to move under the stimulus of a powerful feeder. While it is true that some polsihed forms were taken from the upper levels of this formerly crowded pool, bisque-surfaced forms predominated. With thinning of the population of the pool and acceleration of the feeder the bisque-surfaced forms received a half-polish in a period of just under two years.

Pisoliths and Ooliths with Polyhedral Shapes

The most unusual pisoliths and ooliths taken from Angel Cave, are polyhedral forms faceted in a curiously regular fashion. They were obtained from a pool of small dimensions which, after yielding 1,118 specimens, was still by no means empty. Apart from the usual upper stratum of rather rounded, larger forms, this pool contained a majority of small, angular pisoliths and ooliths. A number of them showed four, five and six facets sufficiently regularly disposed as to simulate simple geometric figures. The facets are commonly concave, often polished at the centre, and their solid and interfacial angles are invariably more or less rounded. In most instances they have bisque surfaces.

A small number of these "geometric" forms have four well-defined triangular faces (Plate I, fig. D, sixth row) resembling tetrahedra. A number have two triangular and three rectangular faces (Plate I, fig. D, seventh row) and are not unlike trigonal prisms, the majority being of squat habit (Plate I, fig. D,

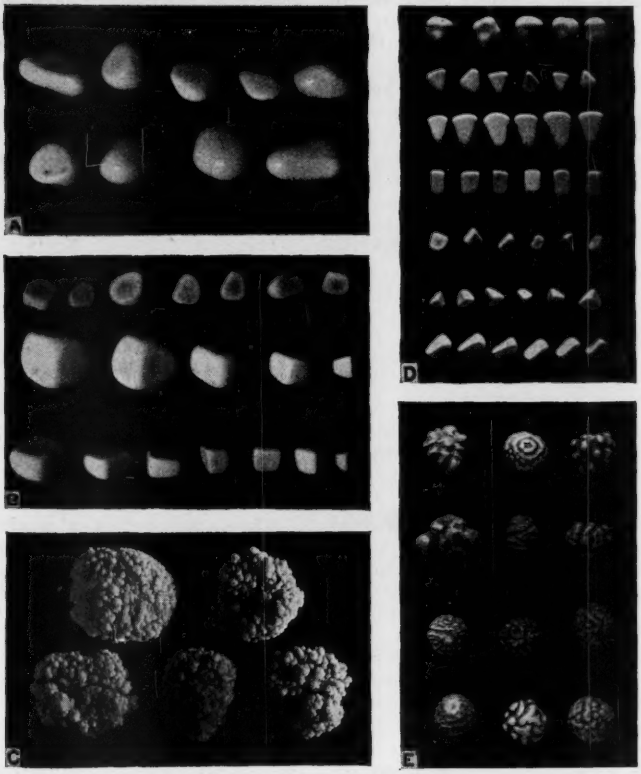

PLATE I. External appearance of cave and mine pisoliths. A to D from Angel Cave, Cape Schanck, E from the Nelson Shaft, Bendigo. (Photographs by A. C. Frostick.)

A—Polished pisoliths ("cave pearls") of varying shape (×1.1).

B—Bisque-surface, polyhedral pisoliths with concave surfaces (×1.6). *Top row*—irregular forms showing dark nucleus (basalt). *Middle row*—wedge-like forms. *Bottom row*—tabular forms.

C—Rough-surfaced pisoliths, showing clusters of radial crystal aggregates (×1.2).

D—Bisque-surface polyhedral pisoliths (×1.2). *Top row*—compound, rounded forms. *Second row*—thin forms with two equilateral triangular faces and rounded solid angles. *Third row*—similar forms with isosceles triangular faces. *Fourth row*—forms with rectangular faces. *Fifth row*—forms with outer surfaces worn through to the dark-colored nucleus (basalt) by rubbing. *Sixth row*—forms with a tetrahedral shape. *Seventh row*—forms with a triangular prismatic shape.

E—Baccate types with pustulose and furrowed surfaces (×1.3).

second and third rows). The remainder show six rectangular faces giving rise to forms of tabular habit (Plate I, fig. B, third row, and fig. D, fourth row), with some of these rather wedge-like (Plate I, fig. B, second row).

Four of the rather less regularly formed polhyedral pisoliths were sectioned, and found to consist of a number of thin, compact, concentric laminae. Two had no recognizable nuclei, and two were built around a nucleus of coarsely crystalline calcite. Of the two latter, the external form of one reflected the shape of the nucleus, while the other one departed very much from the shape of the nucleus.

Some Aspects of the Nature and Growth of the Layering in the Pisoliths from Angel Cave

Illustrative of the asymmetrical disposition of laminae about the nucleus, is a large number of small polyhedral pisoliths obtained from the same pool. These were built around basaltic nuclei, the dark color of which was readily apparent through the thin carbonate veneer at the centre of most of the broader faces (Plate I, fig. B, top row). These curious little forms, with a white border encircling the dark spot in many of their faces, indicate that far from rendering an initially angular pisolith more rounded, as is usually claimed, agitation during the accretion of successive carbonate coatings can, where oscillation is present and free rotation is inhibited by overcrowding, even increase the degree of angularity. It has been suggested that with free rotation, angular pisoliths become rounded because least accretion takes place on projections that are subject to the greatest attrition, but angular forms that undergo oscillatory motion, commonly show least deposition on faces moving in contact with other surfaces, while accretion is unchecked on their free edges.

Asymmetrical accretion also occurs on rough-surfaced pisoliths, because less carbonate is accumulated where the pisolith is in contact with the floor of the containing pool; such contacts are regions least accessible to the feeding solutions. It has been said that when a growing pisolith ceases to be kept in motion by the feeding drip, it will become cemented to the floor of the containing pool. It is improbable that such a process applies to pisoliths in Angel Cave, where it is more likely that cementation would only occur on drying up of the pool waters. Actually no instances of

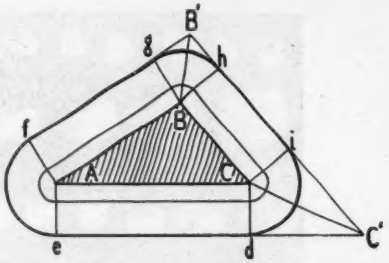

FIG. 4.—Sketch diagram showing an aspect of carbonate growth around a foreign nucleus.

pisoliths cemented to the floors of pools occurred in Angel Cave, although many were cemented to the stalagmitic encrustation covering parts of the cave floor. In this occurrence, however, the evaporating surface of the depositing solution was at the same level as the contact of the cemented pisoliths and their support. Much the same state of affairs would accrue in a drying pool, when the level of the depositing solution was lowered to close proximity with the floor of the pool.

The free movement of a growing pisolith is not the only factor tending to give it a rounded exterior. It can be shown that the accretion of successive layers of even thickness about an angular nucleus, can effect a marked rounding, proportionate to the thickness of the coating.

In the diagram (fig. 4), it is obvious that to preserve the acute angle at C', i.e. an angle that is identical with the

angle *ACB* of the nucleus, more than twice the amount of carbonate must be accumulated in the direction *CC'* as in a direction normal to the faces, at *Ci* or at *Cd*. It is also obvious from the diagram, that the greatest amount of rounding takes place opposite an acute angle. This is observed by comparison of the length of the arc *di* (opposite the acute angle *ACB*), with that of the arc *gh* (opposite the obtuse angle *ABC*). Theoretically, the total length of the flat sides in the expanded perimeter cannot exceed the length of the sides in the perimeter of the nucleus (i.e. $ed = AC$, etc). In other words, with continued expansion of the perimeter of the growing pisolith, the proportion of curved to flat surface must continuously increase. Due to asymmetrical accretion about a motionless pisolith, however, this theoretical proportion may not quite reach its optimum value.

Internal Structures of the Pisoliths

Sliced pisoliths characteristically show concentrically banded layers of calcium carbonate surrounding a nucleus. The pisoliths described by Mackin and Coombs (1945, p. 60) were all said to have a nucleus of some sort of rock or mineral, but many of the Angel Cave pisoliths do not have a foreign nucleus. The nucleus in some consists entirely of calcite crystals precipitated from the pool waters ; the calcite is often coarsely crystalline (Plate II, figs. A and C). In other pisoliths, the nucleus consists of broken fragments of fallen stalactites (fig. 5E), or of small pieces of basalt (fig. 5A-D) washed in from the shingle beach outside the cave, or of quartz grains derived from beach sand; nuclei formed of comminuted marine shells are also known, but are uncommon. Where the nuclei consist of broken stalactites, which in Angel Cave are often tubular and hollow, precipitation of secondary calcium carbonate in the pool waters infills the hollow tubes, as well as encrusting them with concentric layers. The nuclei composed of calcite crystals are consanguineous with the radial and concentric calcite layers. Johnston, Merwin and Williamson (1916, p. 506) showed that in the absence of nuclei in calcium carbonate solutions, the initial precipitate (at temperatures from 15° to 70°) was the μ-form of calcite, so that later growths of calcite develop upon a calcite nucleus. R. C. Emmons (1928) also found that calcite could grow in solutions in which there were no foreign nuclei. It is therefore not surprising to find a considerable number of pisoliths with nuclei of calcite crystals that were formed as initial precipitates in pool waters.

Most of the pisoliths are uni-nucleate (see fig. 5) but types do occur that are multi-nucleate (fig. 5F). Di-nucleate, tri-nucleate, quadri-nucleate and quinque-nucleate examples have been observed. The multi-nucleate forms give rise to the compound types of pisoliths; in them, two to five contiguous grains, each with a few concentric layers of calcium carbonate around them, ultimately become enveloped in one mantle, also usually concentrically banded. Fig. D of Plate II shows a di-nucleate form and fig. B of Plate IV a quinque-nucleate form. The multi-nucleate pisoliths bear a strong resemblance to many of the ferrocalcite amygdales found in the Newer Basalt in the Melbourne District, inasmuch as many centres of growth occur, each with concentric bands of carbonate that become welded with one another at their contacts. Although the ferrocalcite examples are formed from hotter solutions and precipitated in steam cavities in lava, the ultimate internal structure has more than a cursory resemblance to that in cave and mine pisoliths, and the methods of carbonate separation from solution, although rather different, yield similar structures.

The concentric bands of calcite surrounding the nuclei in the pisoliths and ooliths, vary considerably in number from specimen to specimen. Some pisoliths have a very large nucleus compared to the thickness of the enveloping layered crust (fig. 5A and E), while many pos-

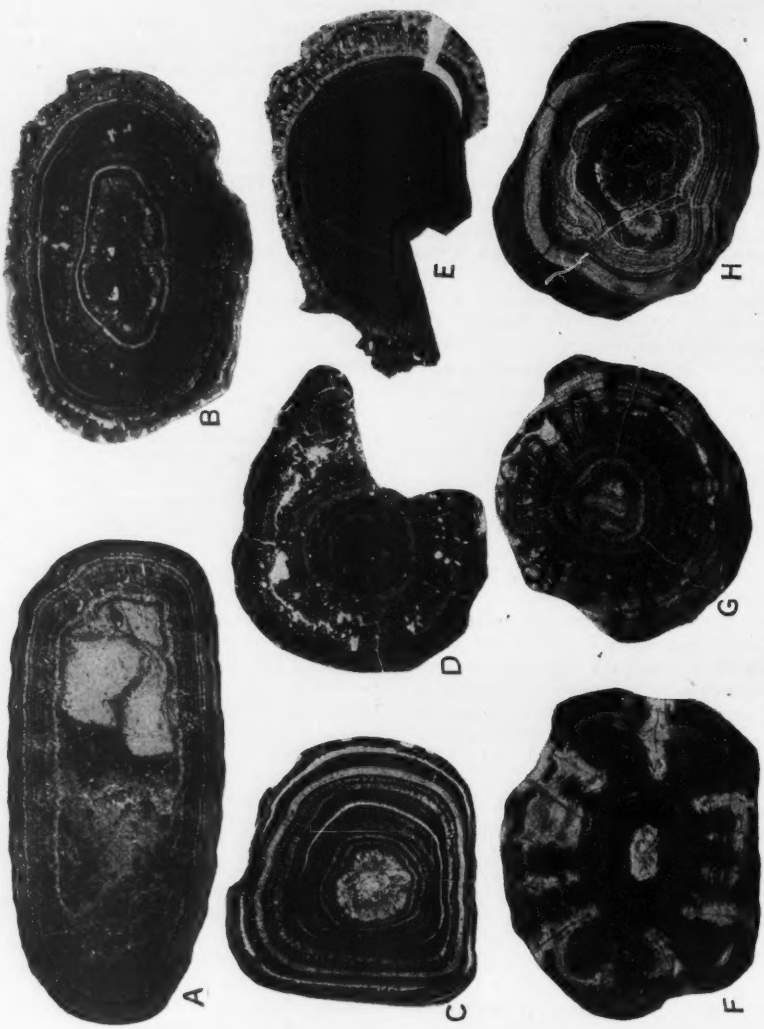

PLATE II. See opposite page for description.

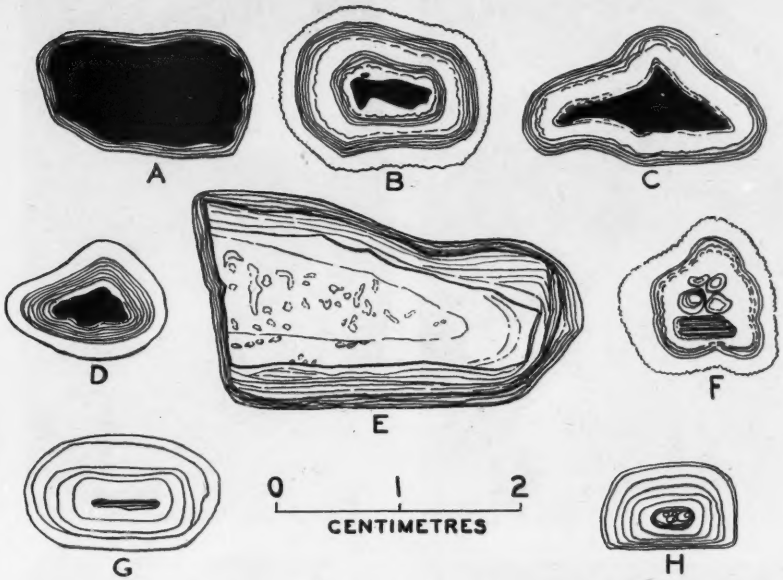

FIG. 5.—Sketch diagrams of nucleate pisoliths. A–D—with basalt nuclei of varying size compared to the thickness of enveloping carbonate layers. E—with nucleus of infilled tubular stalactite fragment. F—multi-nucleate form with five angular and rounded nuclei. G—uni-nucleate pisolith with small fragment of stalactite. H—multi-nucleate pisolith, the nuclei composed of radial calcite growths; later growth by concentric deposition, the layers thinning at the base.

PLATE II. Sliced cave and mine pisoliths. A to E from Angel Cave, Cape Schanck, F to G from Nelson Shaft, Bendigo, H from Central Mine, Broken Hill, N.S.W. (Photographs by Miss M. L. Johnson.)

A—Elongated pisolith with smooth exterior and a nucleus of calcite crystals (×3.85).

B—Ellipsoidal pisolith with rugose exterior and a nucleus of basalt (×4.35).

C—Sub-quadrate pisolith with two faces slightly concave and a nucleus of calcite crystals; thinning of layers in parts (×8.50).

D—Sub-spherical pisolith with two nuclei; each nucleus is a particle of basalt tuff (×4.14).

E—Ellipsoidal pisolith showing concentrically banded inner zone and a broad outer zone of radial growths which form a rugose exterior (×6.26).

F—Ellipsoidal pisolith (baccate type) with a nucleus of slate and complexly interleaved aragonite (dark from artificial staining) and calcite (×10.66).

G—Spheroidal pisolith (baccate type) with complex internal structure due to calcite—aragonite intergrowth (×9.66).

H—Ellipsoidol pisolith, discolored with mine dust and secondary iron and manganese dioxides. Lighter colored layers give a milky opalescence. Spherulitic growths occur in the core around nuclei of iron hydroxide (×3.33).

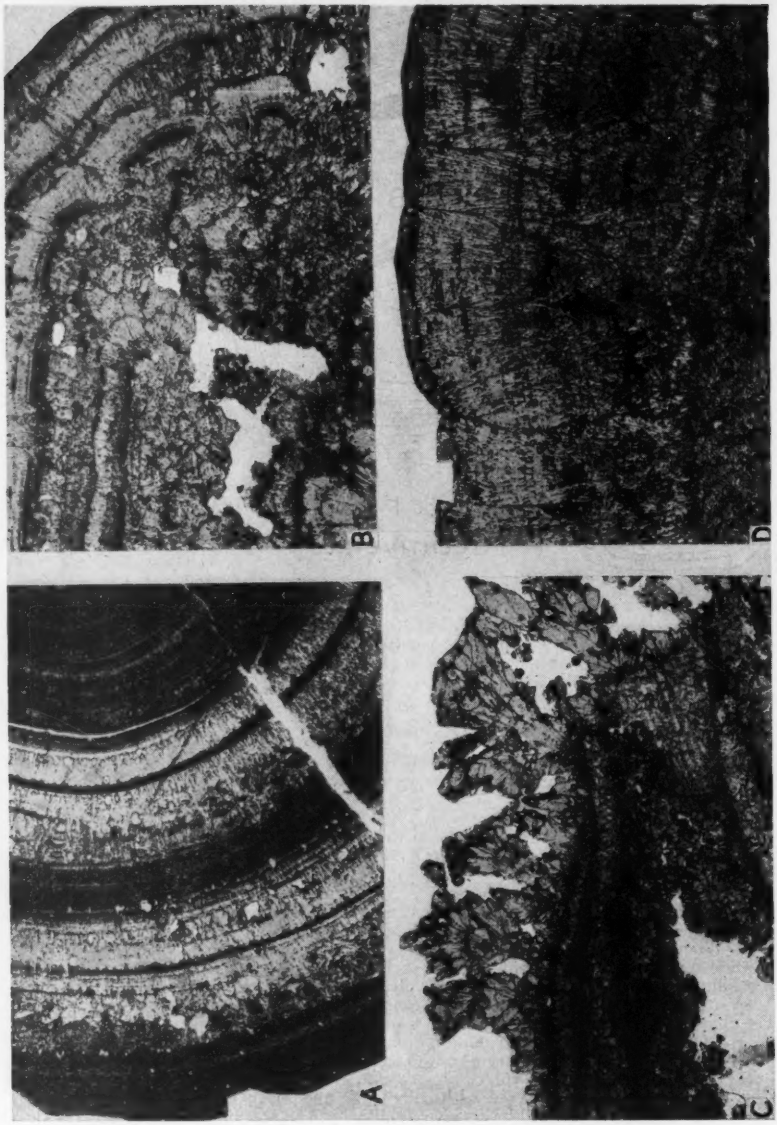

PLATE III. See opposite page for description.

sess a small nucleus and a considerably greater thickness of concentrically banded cover (fig. 5G), which constitutes by far the greater volume of the pisolith. The number of concentric layers varies from three or four up to fifty or so, and their thickness from a fraction of a millimetre up to 4 mm. Plates II and III and fig. 5 illustrate the variation in number, thickness and mode of arrangement of the concentric layers around their nuclei. Layers appearing darker in color in the plates, represent denser (i.e. more highly compacted) bands that have a gray or light brown coloration, while the colorless layers, which are less compacted, invariably show radial growths, with fine, needle-like calcite fibres developed normal to the surface of the preceding layer (Plate IIIA). In the majority of examples, the bands maintain a relatively even thickness throughout. Occasionally, however, the bands are discontinuous (Plate IIIB), the breaks between them being occupied by radial fibres of calcite; the reason for this is obscure. A possible reason for their development is that the discontinuous bands were precipitated on uncompacted layers with a tuberculate exterior. Accelerated drip would cause attrition of the protruding surfaces of tubercle-like projections, upon which compacted layers were deposited. No compaction would develop in the depressions between the tubercle-like processes, and the depressions would then be occupied by radial calcite growths, contiguous with the structure of the uncompacted succeeding layer.

Sometimes the fine, radial growths of calcite are so prominent as to almost completely mask incipient concentric bands, as shown in Plate IIID. The nature of the growth of calcite crystals forming the exterior of rough-surfaced pisoliths like those depicted in Plate IC, is shown in Plate IIIC, where coarse crystals of calcite are formed radially outwards from the surface of the previously-formed concentric band.

These variations in the character of the banding, are undoubtedly a consequence of changes of conditions in the pool waters from which the pisoliths were generated. A feature of the layers with radial fibres of calcite, is the number of small pores present (Plate IIIA). These represent locked-up air, CO_2 or water. Under the highest magnifications, considerable numbers of small "inclusions" are also evident in the bands composed of the coarser radial fibres of calcite. They have similar optical properties to that of the enclosing calcite, but are made evident by having a slightly higher refractive index. These "inclusions" are elongated parallel to the trend of the calcite fibres, assuming the shapes of slender, barbed arrow-heads, with the narrowest end directed away from the centre of the pisolith; some of them are rather more irregular in shape. It is uncertain what the "inclusions" are, or how they were formed, but they are probably a form of calcium carbonate with minor impurities.

PLATE III. Enlarged photomicrographs showing details of internal structures of pisoliths from Angel Cave, Cape Schanck. (Photographs by Miss M. L. Johnson.)

A—Portion of spheroidal pisolith showing regular concentric banding and small pore spaces in zones of radial fibres. Compacted (darker) and less compacted (lighter) bands alternate (×20).

B—Discontinuous banding in internal zones of ellipsoidal pisolith. The breaks in the inner, compacted (darker) bands are occupied by radial growths of calcite (×20).

C—Pisolith with rugose exterior, showing outer zone with coarse, radial growths of calcite crystals (×10).

D—Portion of flat, elongated pisolith, having an uneven surface due to the coalescence of growths consisting of radial fibres; concentric banding poorly marked (×20).

Higher magnifications under the microscope also reveal that many of the concentric bands which appear as one band only under lower magnifications, e.g. the broken bands in Plate IIIB which are 0.7 mm. broad, are actually composed of many thinner bands. Those in Plate IIIB, for instance, consist of approximately 20 laminae, ao that each lamina has an average width of only 0.035 mm.

Murrendal Caves, Victoria

Murrendal Caves are situated about 1 mile north of Buchan in East Gippsland. The occurrence of cave pisoliths here has not been studied in detail, but specimens obtained by W. H. Ferguson, and now lodged in the Victorian Mines Department collection, have been examined. Approximately 90 specimens in this collection consist of rough- and smooth-coated forms, apparently gathered from different pools in the caves. The rough-surfaced forms tend to be spherical in shape, and range in size up to 3 inches across. The rough appearance is due to the development of radial growths of calcite in bunches at regular intervals, most probably under pool water conditions approaching stagnation.

The smooth-surfaced forms are white to creamy-white in color, mostly of rounded character and ranging in size from ¼ inch to 1½ inches across. A few are cylindrical, others somewhat flattened and ranging up to 1½ inches in length. Occasional examples have become highly polished as a result of agitation in pools beneath fast-dripping feeder stalactites. The usual concentrically banded character is evident in sliced examples.

Chillagoe Cave, Queensland

Three examples, lent to us for examination from the collection of Mr. F. S. Colliver, and received by him from Mr. E. E. Pescott in 1930, were found in one of the thirty caves occurring in Lower Palaeozoic limestone at Chillagoe, Queensland. They differ from most other discrete concretions of the pisolith type in each having a hollow nucleus, the nucleus being a univalve shell of the family *Helicidae*. Uncoated examples of this shell occur on the cave earth covering parts of the cave floor.

Jack and Etheridge (1892) in describing this occurrence, stated that on the floor of "The Temple" cave, shells (called *Helix*) occur in all stages of encrustation by lime. The shells were said to be plentifully scattered over the floor in places, and such parts were regarded as probably being the sites of pools in wet weather. Some of the shells had become cemented into the calcareous encrustation on the cave floor.

The shells act as nuclei for the precipitation of calcium carbonate from calcareous solutions dripping from the roof of the limestone cave. Three stages shown by the specimens under discussion are:—(i) partially encrusted shell, with aperture and umbilicus still open, (ii) encrusted form with aperture and umbilicus closed, but with marked depression in the aperture region, and (iii) completely encrusted form with little evidence remaining to mark the original position of the aperture.

In the second stage, partial polishing of the smooth surface of secondary calcium carbonate points to agitation in a pool on the cave floor, probably during the wet period when feeder sources from the roof provided a more rapid supply of calcareous waters. The third stage shows later encrustation by radial out-growths of calcite, formed during a period of slow supply of solutions and almost stagnant conditions in a pool prior to drying up.

Precipitation of $CaCO_3$ on the shells, as evidenced in a sliced example (stage iii above), was first by concentric deposition all along the exposed outer surface of the shell and on the inside walls of the aperture. Later precipitation, forming the outer, rough-surfaced zone, was by radial growths, which, in the aperture and umbilical regions, united across gaps to completely close up the openings. The inner walls of the inside chambers of the shell did not become encrusted, while a

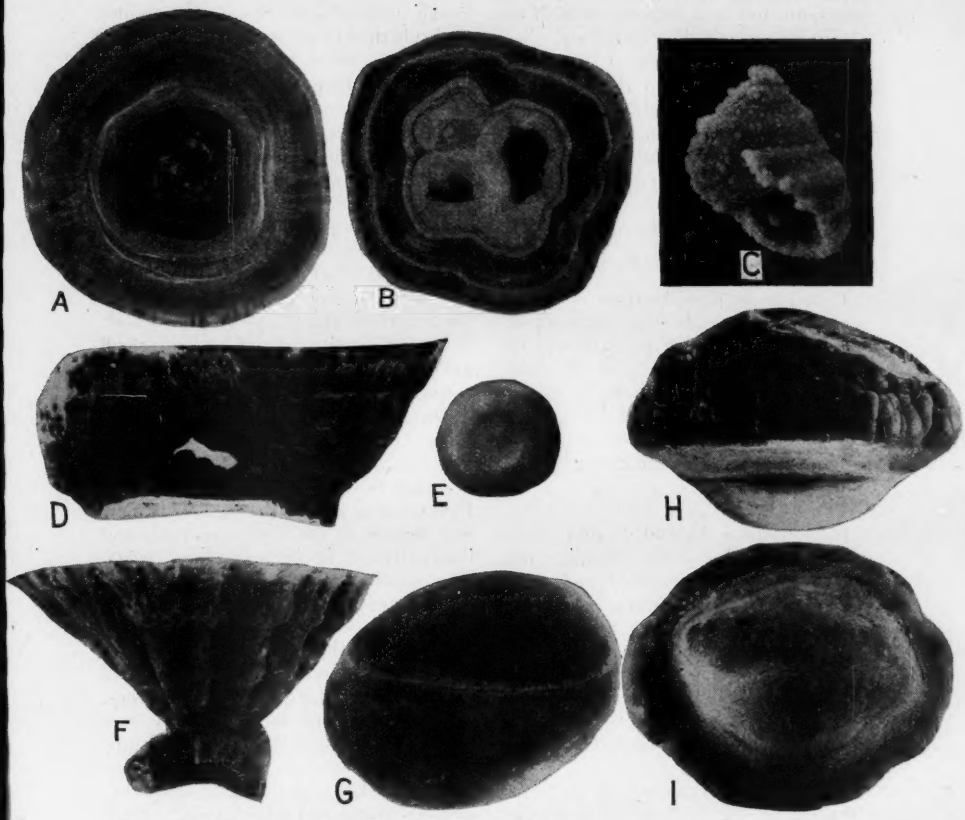

PLATE IV. (Photographs by Miss M. L. Johnson.)

A—Sliced and polished pisolith (×3), Central Mine, Broken Hill, N.S.W.

B—Quinque-nucleate pisolith (sliced and polished) (×3), Central Mine, Broken Hill, N.S.W.

C—Carbonate encrusted marine shell (*Monodonta*) (×2), Angel Cave, Cape Schanck, Victoria.

D—"Coral-like" growth (×3), Central Mine, Broken Hill, N.S.W.

E—"Cave pearl" type of pisolith with concavity (×6), Shinano Province, Honshiu Is., Japan.

F—"Coral-like" growth (×3), Central Mine, Broken Hill, N.S.W.

G—Basalt pebble showing "plimsol line" of carbonate deposit, from pool in Angel Cave, Cape Schanck (×½).

H and I—Side and bottom aspects of elongated pisolith showing additional growth on top (×2), Central Mine, Broken Hill, N.S.W.

small shell (youthful stage) of the same genus occurred inside the adult form. It was quite free and with no signs of encrustation by secondary carbonate.

The mode of formation of these types is essentially similar to the growth of pisoliths as discrete calcareous concretions in caves. In them, a hollow shell acts as a nucleus for the concentric and radial growth of secondary calcium carbonate from the calcareous waters contained in pools on cave floors.

Section B.—Mine Pisoliths

Examples of pisoliths from mines are generally comparable in appearance, structure and mode of formation to the round and ellipsoidal cave pisoliths. Some of them include small amounts of mine dust, some are discolored by iron and magnanese hydroxides to greater extents than is usual with cave pisoliths.

Bendigo, Victoria

In Johnson's Extended gold mine, Garden Gully line of reef, Bendigo, one occurrence of pisoliths was found about 100 feet below the surface (i.e. above groundwater level), while another was found 500 feet below the surface of the ground. Similar pisoliths to these have also been observed in mines on the Hustler's line of reef and in the Great Northern mine on the Garden Gully line of reef at Bendigo.

The samples examined by us were collected by F. L. Stillwell sometime between 1916 and 1918, from the floors of disused crosscuts put in 40 to 50 years previously. One or two nests of pisoliths occurred in depressions on the floors of each of the crosscuts, where carbonate waters dripping slowly from the roofs, had hardened portions of the floors below by depositing secondary $CaCO_3$. The atmosphere in the crosscuts was practically stagnant and the temperature relatively constant. The $CaCO_3$ was derived from Ordovician sediments that include rare "cone in cone" limestones.

The pisoliths are white to creamy-white in colour, and mainly have bisque surfaces. A few have developed a good polish, and some exhibit occasional rough-surfaced areas. Shapes are rounded and spherical to ellipsoidal, and the sizes range from 13 to 19 mm. across. Occasional examples exhibit two to three concentric ridges on the outer surface, indicating changes of water level in the pools where they were generated. Sliced specimens show fine, concentric banding, with up to as many as three dozen layers. These have been accumulated around irregularly-shaped nuclei consisting of quartz and other matter foreign to the pisoliths. The specific gravity of one of the relatively well-polished forms is 2.76, indicating calcite, probably with small amounts of $MgCO_3$ which occurs in mine waters to some extent.

Departures from the normal types of mine (and cave) pisoliths have been found in the Nelson shaft (subsequently renamed Johnson's No. 3 shaft), on the Derby line of reef at Bendigo. This mine was worked in the 1860's, in 1916, and intermittently in between these years. The pisoliths are much smaller than those generally found in the other Bendigo mines, averaging 5 to 6 mm. in diameter for the more or less globular forms, and 5 mm. by 7 mm., rarely 7 mm. by 9 mm., for the ellipsoidal types. The pisoliths differ in having their surfaces regularly studded with round protuberances, imparting to them a *baccate* (i.e. berry-like) appearance. A few, however, are fluted and ridged, being Chara-like in character (Plate I, fig. E). They are usually brownish-gray in colour, and have a specific gravity of 2.78. This value, being greater than that for calcite (2.714), suggests the presence of some aragonite and probably small amounts of $MgCO_3$. A positive test obtained by means of Meigen's reaction, confirmed the presence of some aragonite. The rounded protuberances and ridges occasionally have their most exposed surfaces somewhat buffed, indicating agitation against the neighbouring pisoliths in the pools. Thin films of mine dust, and a minor amount of siderite, occur in the

depressions between the rounded protuberances. Mr. Baragwanath, of the Victorian Mines Department, informs us that these types develop in a very short period of time; their period of formation ceases rapidly as the mine waters become diverted by new mining activities.

The complexity of growth is indicated in Plate II, figs. F and G, where the dark areas in fig. F are probably sideritic, while darker areas in fig. G are partly a result of the stain (artificial) taken up by aragonite.

St. Arnaud, Victoria

In a drive below No. 2 level in the Lord Nelson mine at St. Arnaud, pisoliths are very much like those from the Nelson shaft at Bendigo. They are relatively common from this level. (A large number of them is stored in the Victorian Mines Department collection.) Some of these pisoliths have been agitated to such an extent in the pool waters, that constant buffing has removed most of the protuberances from some examples to produce smooth-surfaced forms.

Harrietville, Victoria

Some 60 or so pisoliths were collected by J. P. L. Kenny from Old Drive, Mons Meg mine, Harrietville, and are now in the Victorian Mines Department collection. The forms vary in size from ¼ inch to 2 inches long and are of irregular shape. They are flesh-colored to white in color, and mostly possess bisque surfaces.

Ballarat, Victoria

We have been informed by Mr. Baragwanath that calcareous concretions like the pisoliths under discussion, were "scooped out in handfuls from pools" in some of the old Ballarat mines. Water pipes used in mining activities underground at Ballarat became infilled in a very short time, in places where carbonate-rich waters were copious. Such calcareous accumulations were referred to by Baragwanath (1923) as travertine.

The analysis (Baragwanath, 1923, p. 61) is set out in Table 6.

TABLE 6. *Analysis of calcareous encrustation from the deeper levels of the Ballarat gold mines*

$CaCO_3$	—89.33%
$MgCO_3$	— 5.53%
$FeCO_3$	— 0.59%
Insoluble	— 0.43%
TOTAL	—96.38%

(The amount of water present was not determined.)

The percentages of magnesium and iron carbonates are considered adequate to raise the specific gravity values for such encrustations and allied pisolithic growths, and a similar state of affairs may thus account for the higher specific gravity values met with in some of the pisoliths in the Bendigo mines.

Samples of the pisoliths from the Ballarat mines were not available for examination. It is quite probable that many other mines, both in Victoria and elsewhere, would yield specimens of pisoliths where searched for.

Broken Hill, New South Wales

Pisolithic growths of calcium carbonate are known from the Central Mine (lead-zinc) at Broken Hill in New South Wales, where they are formed by deposition from solutions dripping from the roof into pools on the floor of a drive in the mine.

The pisoliths vary in color from white to light brown, according to a small variable content of iron carbonate. They are commonly of the bisque-surface type, with occasional well-polished examples of the "cave pearl" type. Rounded shapes predominate; a few specimens have shallow, concave facets resulting from crowding in the pool and rubbing against neighbors on agitation. None of the concave facets, however, approaches the degree of perfection developed in small pisoliths from Shinano Province, Honshiu Island, Japan (see Plate IV, fig. E).

Forms with smoothly pustulate to rough surfaces are uncommon. The range

in size is from 7 mm. to 18 mm. across. One of oval shape (see Plate IV, figs. H and I) is 30 mm. by 22 mm., and 18 mm. deep; it has grown more extensively on one half as a result of the operation of the "plimsol line" effect (cf. Plate IV, fig. G). Greatest deposition occurs at water level in pools, and this specimen indicates growth additions of carbonate as concentration of carbonate increased while water level fell on evaporation. The specimen was collected before the pool had completely dried up, hence the "mushroom-like" shape of the pisolith.

Concentric growth bands are well-marked in the Central Mine pisoliths, as indicated in Plate IV, figs. A and B; the radial markings in the illustration (Plate IV, fig. A), are observed to lead to the outer surface where small, papillose elevations occur. Growth of the concentric bands is initially around either a single nucleus, sometimes of quartz, sometimes of rhodonite, or around several foreign particles, resulting in the formation of multi-nucleate examples like that in Plate IV, fig. B (a quinque-nucleate pisolith). The multi-nucleate type has arisen from the union of several small forms developed in close proximity. Other types of calcareous growths developed attached to the mine floor at Broken Hill (Central Mine), resemble single corals (Plate IV, figs. D and F). They are of rarer occurrence than the pisoliths, and are principally in the nature of radial growths upwards and outwards from an attached base.

Origin of Pisoliths and Ooliths as Discrete Concretions

The pisoliths and ooliths examined from the Australian caves and mines were all precipitated by physico-chemical rather than by biochemical agencies. Investigators searching for evidence of the existence of organisms dwelling in the pools containing the calcareous concretions in Angel Cave, found that the pool waters contained no life, only mineral matter (Melhuish and Deane, 1937).

R. C. Emmons (1928) showed that by simple saturation on cooling, minute $CaCO_3$ crystals could grow regardless of whether nuclei were present. He also concluded from his experiments, that contact of air with water saturated with calcium bicarbonate, effectively precipitated $CaCO_3$ by removing CO_2 from solution, and that agitation had a similar effect. Although the question of temperature changes has little bearing on the deposition of $CaCO_3$ in the pools in Angel Cave, it is of importance to note that Emmons found that foreign nuclei were unnecessary for initial growth. Many pisoliths formed in Angel Cave have no visible foreign nucleus, the centres often consisting of calcite crystals, and so these types can have been formed initially in some such manner as that advocated by Emmons, with agitation rather than temperature changes being the more important factor. The effect of reduction of gas pressure, well beyond any reduction likely to occur in nature, was found by Emmons to have a very small effect upon the precipitation of $CaCO_3$, and this factor is negligible in Angel Cave.

Linck (1903) recorded that all the recent ooliths he examined were composed of aragonite, whereas older, fossil occurrences were of calcite. Hatch, Rastall and Black (1938), however, state that "cave pearls" are exceptional among recent pisoliths in consisting of calcite rather than aragonite, a difference which they regard as attributable partly to the low temperature at which precipitation occurs, and partly to the low content of salts, other than the calcium carbonate, in the precipitating solution. Now such exceptions are not to be confined to "cave pearls," if this term is reserved specifically for the polished varieties of cave pisoliths, but also applies to the other varieties of pisoliths and ooliths such as the bisque-surface and rough-surface varieties found in both caves and mines. These are composed principally of calcite, although some of the examples from mines in Australia, do contain a proportion of aragonite as well.

The time taken for the pisoliths to form in Angel Cave, Cape Schanck, Victoria, is unknown, but the rate of formation must be rather rapid on parts of the cave floor subject to marine invasion. Mackin and Coombs (1945, p. 58) arrived at a figure of 35 to 42 years for the period of formation of pisoliths in a mine in Idaho, U. S. A. A similar length of time is indicated for their development in mines at Bendigo, Victoria, where some 40 years or so had elapsed from the time of the opening of the mine to the time of collection of the pisoliths. They may have been formed in a shorter period of time here, however, because they may have been well-developed and might have ceased growing some time before they were collected; moreover, the particular drive in which they were found, was opened up some time after the original underground workings were commenced. It would seem that the formation of pisoliths in some of the mines at Ballarat, Victoria, occupied periods of time to be measured in months rather than in years, according to the statements of the Director of the Geological Survey of Victoria (Mr. Baragwanath), who observed the rapid accumulation of secondary calcareous growths in some of the mine drives at Ballarat.

Bucher (1918) advanced the view that pisoliths and ooliths are to be regarded as due to colloidal precipitation, and are to be interpreted, as Schade (1909 and, 1910) has interpreted the urinary calculi and concrements with allied structures, as concretionary bodies which are due to the solidification of an emulsoid. During this process, a change towards the crystalline state is said to occur, and a radial structure develops if the substance is pure. If other substances have been precipitated along with it, however, a concentric structure is produced. The authors believe that the growth of the pisoliths as discrete bodies in cave and mine pools, is not to be ascribed to precipitation from the colloidal state. Colloidal $CaCO_3$ can be obtained in the laboratory, but only with very high concentrations of $CaCl_2$ and $NaCO_3$, far higher than is likely to be met with under natural conditions in pools in limestone caverns and in mines.

Changes in the internal structures of the pisoliths, from bands of radial growths, to bands of concentric growths, are due to interruptions affecting the continuity of deposition of either particular growth type. Such changes were frequent during the growth of an average size pisolith, hence, the interruptions must be due to some periodic phenomenon (or phenomena). The changes of conditions must have been sudden, as evidenced by sharp, definite contacts between the bands. Bryan (1941, pp. 49–50) found similar such changes in spherulitic structures built up of radial and concentric growths. He regarded the interruptions as resulting from slight pauses in crystallisation, due probably to rapid crystallisation bringing the immediate source of supply down to saturation point. Crystallisation was resumed as soon as diffusion of supplies through the surrounding medium had brought about the necessary concentration.

Applying similar arguments to the formation of pisoliths, during the development of which interruptions occurred in growth structures built up of only one mineral substance ($CaCO_3$), it would seem that the sharp discontinuities between the bands, indicate pauses in crystallisation resulting from changes in the rate of supply of nourishing solutions. The rate of supply would vary according to the oncoming of wet periods, when a more abundant supply of water diluted the calcareous solutions. As a consequence, conditions in the pool waters were reduced below saturation, crystallisation practically ceased, and a disturbed period ensued, causing buffing and polishing of pisoliths.

With diminution of water supply in drier periods, evaporation became dominant in the pool waters, and a stage was eventually reached when the pool waters were saturated with calcium carbonate. Crystallisation followed, but only slowly,

as evaporation kept pace to maintain saturation. Coarser calcite crystals produced during this phase, led to the formation of the broader bands showing radial growths. This period of growth would be one in which the pool waters remained in a relatively undisturbed state, so that no buffing or polishing of the outermost growth layers could occur. If, at the onset of saturation conditions, crystallisation failed to develop for some reason, the pool waters would ultimately reach a state of supersaturation, when sudden crystallisation set in and continued until a state of saturation was again attained. During this period of growth of the carbonate layers, the pool waters again remained undisturbed, and concentric bands composed of numerous, narrow layers, each with small, fine calcite crystals were developed. The operation of these processes would satisfactorily explain the sharp discontinuities between the several bands, the variations in structure of the layers and the development of polished surfaces on some inner layers.

The origin of the shapes and polished character of certain of the pisoliths, is a matter of some controversy. Hess (1929) believed that the agitation of the water in pools, caused by the splash of falling drops, was sufficient to keep the pisoliths contained therein, on the move during their growth, and so they remained more or less spherical. Hatch, Rastall and Black (1938) regarded the "cave pearl" variety of the pisoliths as being formed in pools and streams where the water motion was sufficiently vigorous to roll over the growing concretions, so that deposition was more or less even on all sides. They advocated vigorous agitation of nuclei in a solution which was actively precipitating calcium carbonate.

W. H. Emmons (1928), however, had not accepted the idea of rolling around of the pisoliths during deposition, and thought that the carbonate was added layer by layer around a nucleus. As a result, fragments would be gradually lifted up by the force of crystal growth, because, he stated, the water was not agitated and the fragments were flat and had not rolled over.

From experiments and from their observations of "cave pearls" in all stages of growth under natural conditions, Davidson and McKinstry (1931) were convinced that rolling during carbonate deposition was not necessary. They found by experiment that a layer of $CaCO_3$ 1 to 2 mm. thick, grew in 1½ years around a nucleus (a fragment of andesite) placed in a mine pool of nearly stagnant solution. Growth of this layer lifted the fragment against the force of gravity from its original position. They also found that the carbonate layer on the underside of the fragment was a fraction thinner than on the sides and top, but the form remained unattached. If the rate of growth indicated by Davidson and McKinstry more or less holds under the conditions prevalent in Angel Cave, then the larger pisoliths contained therein took some three or four years to reach the size attained at the time they were collected.

In pools in Angel Cave, evidence exists that rocking and rolling about of pisoliths does occur, even though such motions may not be essential for their growth. In a few pools, many of the pisoliths leap about under fast dripping feeder stalactites. The rocking and rolling motion undoubtedly suffices to prevent fixation of the pisoliths to the walls and floors of the pools. So also does gentle circulation of seepage waters that find their way into pools where the pool water is not strongly agitated by drips. Mackin and Coombs (1945) found similar evidence in a mine in Idaho, U. S. A. They proved that rotation did occur in pools where visible agitation was not strongly evident; one pisolith, which was marked, was seen to rotate ¼ turn every 2 minutes. Casteret (1939) also noted a perpetual rolling of "cave pearls" in a natural cavern in France, but Lee (1925) and Hess (1929) noted only a slight rocking motion of the "cave pearls" in "nests" in the Carlsbad caverns, New Mexico, U. S. A.

Observations in Angel Cave, Cape Schanck, show that with fast-dripping water supply, pisoliths up to 15 mm. across leap about in the pool waters, while larger ones, up to 33 mm. in length, rock to and fro. Under less strongly dripping feeder stalactites, the motion of the pisoliths is far less evident, and in pools containing stagnant waters, appears to be negligible. Nevertheless, even in pools into which no water drips from the cave roof, the more or less constant seepage of calcareous waters across the cave floor suffices to keep the pool waters in slow circulation and gives rise to a slow overflow.

Evidence of rolling over of pisoliths during growth is provided by the example depicted in Plate II, fig. C, where thinning of layers is to be seen on the left-hand side, half way between the nucleus and the outer surface. The pisolith at this particular stage of growth was in a position comparable to the stage of growth at the time of collecting, i.e. the flatter face formed the base, where constriction of some layers is again evident. Inhibition of the growth of some concentric layers in such positions is partly due to slightly decreased supply to the face of the pisolith in contact with the bottom of the host pool, and partly to agitation during deposition.

It is during the leaping, rolling and rocking to and fro motions that the surfaces of pisoliths become polished, giving rise to the "cave pearl" types. The shapes of the pisoliths also help to determine the continuity of polish over their surfaces. Examples with irregularities obviously only have the exposed surfaces of the protuberances well buffed and polished, unless occurring in pools with many, much smaller pisoliths and ooliths, under which circumstance, the hollows of larger pisoliths may also become buffed and polished. The fact that several rough-surfaced pisoliths, on being broken along the concentric layers, reveal inner zones, some with highly polished and some with bisque surfaces, plainly provides evidence of change of rate of drip from time to time during pisolith growth. The polished surfaces indicate periods when drip was strong, bisque surfaces indicate less rapid drip, while nodulose and rough-surface examples (Plate I, fig. C and Plate II, fig. E) generally indicate slow drip or even almost stagnant conditions in the pool waters. Although there is a certain periodicity thus indicated during the growth of the pisoliths, there is no means of ascertaining the significance of the periodicity in terms of any ordered repetition of seasonal variations.

The rounded and ellipsoidal shapes, so common among pisoliths and ooliths, are controlled partly by (1) buffing effects, with rounding of irregularities and nodes, consequent upon strong to vigorous agitation in pools in caves and mines, partly by (2) the shape of the original nucleus around which concentric and radial deposition takes place, also the thickness of the coating precipitated on the nucleus, and partly by (3) the degree of crowding in any given pool. Pisoliths in pools with a low population, generally attain rounded and ellipsoidal shapes. In densely populated pools, where larger forms occur in the upper levels, and the smallest in the lower levels of the pool water, a considerable variety of shapes is encountered.

CONCLUSIONS

The results of the foregoing investigations reveal that it is not essential to have foreign nuclei present in cave pools for the precipitation of calcium carbonate as pisoliths, although their presence stimulates precipitation in some instances.

Rolling around of pisoliths and ooliths in cave pool waters is essential for the buffing and polishing leading to the development of the "cave pearl" varieties, but is not necessarily essential for bisque-surfaced types, and must be lacking for the formation of rough-surfaced types. Whereas agitation accompanied by free rotation will produce "cave pearls," agitation, where free rotation is inhibited by crowding, will produce poly-

hedral forms. Moreover where crowding is acute, a percentage of "geometric" forms may appear, particularly when a supply of angular nuclei is available so that free rotation is curbed at an early stage in their development.

Buffing of the carbonate layers during their deposition results in greater compaction, thus leading to layers with structures markedly different from the more crystalline, porous layers that grew when fed by waters circulating through seepage rather than through disturbance by strongly dripping overhead feeders. Variations in degree of agitation of pool waters during the growth history of the pisoliths, is clearly indicated by the alternations of less compacted and more highly compacted layers. The sharp lines of demarcation between the various layers show that marked pauses occurred during their development. The constituent fibres of the more highly compacted layers are smaller and are radial to the centre of the pisolith, those in less compacted layers are larger, and although they also develop radial structures, these generally form about a number of local centres, bunched around a common focus.

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FIG. 1, AUGUST, 1947

TRINITY SEDIMENTS OF NORTH AND CENTRAL TEXAS

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ABSTRACT

The Trinity group, except in Red River area, is divided into three stratigraphic units which in ascending order are Travis Peak or "Basement Sands," Glen Rose limestone, and Paluxy sands. The coarse-grained clastics, larger than $\frac{1}{16}$ mm., are characterized by texture, degree of abrasional wear, and heavy mineral assemblages. The fine-grained materials, the silt and clay sizes, constitute about 50 per cent of some of the deposits. The limestones were analyzed for carbonates and insoluble residues.

INTRODUCTION

Exposures of Trinity sediments in north and central Texas extend from Red River, Montague County, southward to Hood and Somervell counties where they swing westward across the Callahan Divide to Nolan County. The sediments were deposited in a sea which spread progressively westward over Pennsylvanian and Permian strata.

The Trinity of the lower Cretaceous, except in Red River area, is divided into three stratigraphic units which in ascending order are Travis Peak or "Basement Sands," Glen Rose limestones, and Paluxy sands. As the Glen Rose limestones are not represented in Red River area, the upper and lower sands constitute a depositional unit which is known as "Antler Sands."

The sediments in Travis Peak formation grade upward from basal conglomerates into sands and clays. The conglomerates are about three feet thick, consolidated, and consist chiefly of well rounded quartz pebbles and cobbles in a matrix of sand and clay. The sands and clays are unconsolidated, varicolored and range in thickness from 75 to 250 feet. The red and yellow materials, chiefly clay particles, are readily removed by washing. The Travis Peak is a well developed unit in Parker, Erath and Comanche counties: to the north it is a part of the Antlers Sand: to the west it thins and finally disappears before reaching the Callahan Divide.

The Glen Rose limestones are well developed in southern Parker County (Scott, 1930) and at the type section, Paluxy River, Somervell County (Hill, 1891), but to the north and west they grade into sands and clays. The limestones are gray to brown, resistant, fossiliferous, medium to thin-bedded, interlensed with layers of sand and clay, and attains a maximum thickness of about 200 feet.

The Paluxy sands represent a stratigraphic unit in the exposures south and west of central Wise County. The sediments are vari-colored (white predominating), unconsolidated and attain a thickness of 160 feet. West of Brown County the Paluxy is the only representative of the Trinity group and consists of basal conglomerates which grade upward into coarse sands interlensed with thin, discontinuous layers of clay.

Exposures in each of the counties were visited to learn the general characteristics of the strata and to collect materials for laboratory study. Samples from each locality represent a vertical cross-section of the deposit. About 25 grams of each sand sample were analyzed in the laboratory for texture, degree of abrasional wear, mineral content, inclusions, and degree of alteration. The quantities of carbonates and insoluble residues in the limestones were secured by digesting 50 gram samples in a .5 normal solution of hydrochloric acid.

CHARACTERISTICS OF THE SEDIMENTS

Some of the distinguishing characteristics of the Trinity sediments are texture, degree of abrasional wear, heavy mineral assemblages, carbonates, insoluble residues, and properties of the minerals. The clastics are divided into coarse-grained, larger than 1/16 mm., and fine-grained, silt and clay sizes. Extending south and west of Red River to Erath County, the maximum size grade of the coarse-grained sediments is 1/16 to 1/8 mm.: west of Erath County the maximum size grade increases to 1/8 to 1/4 mm. (table 1). Percentages of fine-grained clastics, about 50 per cent of the deposits in Parker and Erath counties, decreases northward to 36 per cent in Montague County and westward to 14 per cent in Taylor County.

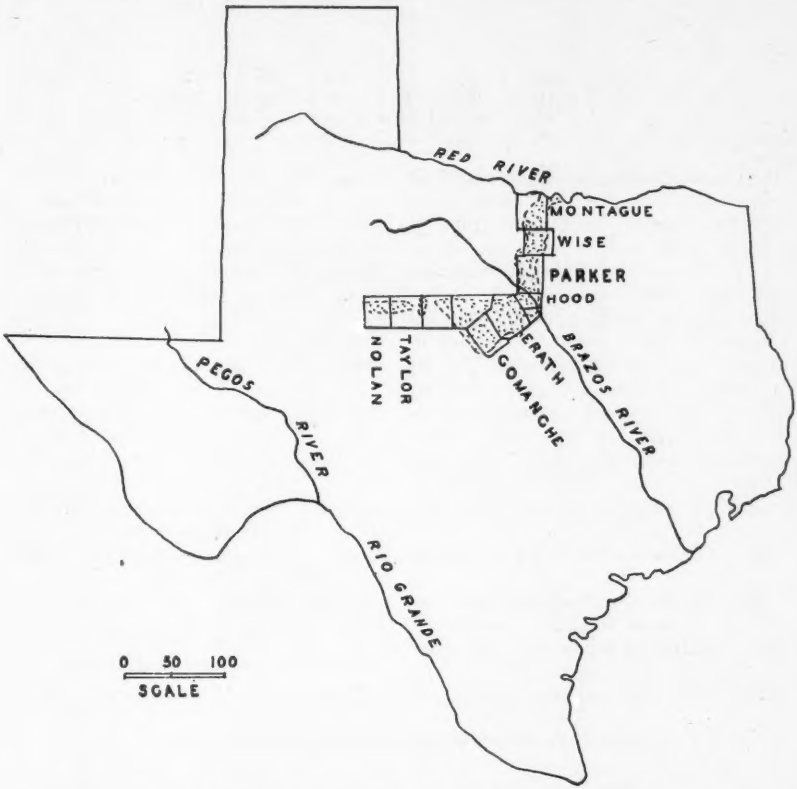

FIG. 1.—Map showing general distribution of Trinity sediments.

The degree of abrasional wear was determined by counting the rounded, sub-angular, and angular grains of quartz, tourmaline, zircon and rutile in sizes less than 1/4 mm. About 40 per cent of the grains of quartz, zircon, and rutile are rounded, 40 per cent sub-angular, and 20 per cent angular, whereas, 50 per cent of

TABLE 1. *Showing size grades of Trinity sediments*

County	Montague	Wise	Parker	Parker	Erath	Erath	Comanche	Taylor	Nolan
Formation	Antlers	Antlers	Travis Peak	Paluxy	Travis Peak	Paluxy	Travis Peak	Paluxy	Paluxy
−1								.8	5.2
$-\frac{1}{2}$	.5	3.1	.9	.6	.3	.2	3.1	30.7	33.2
$-\frac{1}{4}$	15.4	14.7	5.2	3.4	9.3	15.8	57.7	44.6	50.8
$-\frac{1}{8}$	45.7	41.9	38.0	38.2	36.4	30.6	24.9	8.3	2.3
$-\frac{1}{16}$	38.4	40.3	55.9	57.8	54.0	53.4	14.3	15.6	8.5

the grains of tourmaline are rounded, 30 per cent sub-angular, and 20 per cent angular. Most of the rounded grains of quartz are frosted, a few are pitted.

The abundance of heavy minerals, per cent of each mineral with respect to total number, was obtained by counting (Table 2). The mineral assemblage in Trinity sands is characterized by an abundance of tourmaline, ilmenite and zircon: slightly smaller quantities of rutile, magnetite and leucoxene: minor quantities of staurolite and hematite: and a few grains of garnet. The abundance of magnetite, ilmenite, and hematite decreases from east to west, whereas staurolite and zircon show a corresponding increase.

The limestones in the Glen Rose formation are dense, light gray, interlensed with thin layers of yellow clay, and attain a maximum thickness of 240 feet. The beds have a wide horizontal extent and range from less than one inch to three feet in thickness. The mineral constituents of the limestones were determined from thin sections. These show that the the ground-mass, about 10 per cent of the rock, consists of small crystals, probably calcite, and clayey materials. The minerals that can be identified consist of calcite, dolomite and a few sand grains.

The carbonates, representing the difference in weight of the original materials and the insoluble residues, range in quantity from 82 to 89 per cent of the rock. The insoluble residues consist of clays and a few mineral grains which are similar to the mineral constituents of the sands. The clays are greenish-gray, range in quantity from 10 to 16 per cent of the rock and consist chiefly of montmorillonite minerals and a few glass shards.

PROPERTIES OF THE MINERALS

Tourmaline—Three varieties of tour-

TABLE 2. *Percentages of heavy minerals in the Trinity sands*

County	Montague	Wise	Parker	Parker	Erath	Erath	Comanche	Taylor	Nolan
Formation	Antlers	Antlers	Travis Peak	Paluxy	Travis Peak	Paluxy	Travis Peak	Paluxy	Paluxy
Tourmaline	23.9	26.7	33.7	28.3	33.2	44.1	19.7	23.2	33.5
Ilmenite	24.6	24.2	31.0	23.9	18.8	20.5	27.1	13.2	13.6
Zircon	18.2	15.2	9.2	14.9	18.9	13.6	22.1	28.5	25.0
Rutile	10.7	12.1	6.3	11.1	9.2	9.4	7.5	10.8	9.3
Magnetite	8.4	9.1	11.4	10.9	7.4	4.7	7.6	3.9	3.2
Leucoxene	9.1	6.6	4.4	7.3	7.1	5.1	3.3	5.1	7.9
Staurolite	1.8	1.6	1.0	1.4	1.2	1.0	6.2	12.2	6.3
Hematite	3.0	2.8	.2.0	2.2	2.8	1.6	2.0	1.1	1.2
Garnet	.3	1.7	1.0		1.4		4.5	1.9	

maline; black, brown and blue, are represented. These occur as prisms with basal terminations, well rounded grains, and irregular fragments. Opaque minerals, slightly elongated gas bubbles, and transparent acicular inclusions are numerous. The abundance of tourmaline ranges from a maximum of 44 per cent of the heavy minerals in Erath County to 19.7 per cent in Comanche County: the average for all localities is 28.8 per cent.

Ilmenite—The abundance of ilmenite decreases from a maximum of 28.4 per cent in Parker County to 13.2 per cent in Taylor County. About 42 per cent of the grains of ilmenite are rounded, 40 per cent sub-angular, and 18 per cent angular. Ilmenite is characterized by the iron black color, steel gray luster, and crimson sheen. Some of the grains are partly altered to leucoxene.

Zircon—The occurrence of zircon is about equally divided between euhedral and rounded grains. These consist of two varieties, transparent and mauve, which are concentrated in sizes less than $\frac{1}{8}$ mm. Gas bubble and rod-like transparent mineral inclusions are numerous. Maximum abundance of zircon, 28.5 per cent of the heavy minerals, is in the Paluxy sands of Taylor County but the average for the Trinity sands is 18.7 per cent.

Rutile—Rutile occurs as rounded grains and irregular fragments. It is characterized by the high index of refraction, faint pleochroism, and red to brown colors which do not change under crossed nicols. The abundance of rutile is uniform throughout the Trinity sands, making up about 10 per cent of the heavy minerals.

Magnetite—Magnetite constitutes about 6.8 per cent of the heavy minerals. It decreases in abundance from a maximum of 11 per cent in Parker County to 3.2 per cent in Nolan County. Magnetite occurs chiefly as shiny black grains of which 40 per cent are rounded, and 20 per cent fragmental. Some of the grains are partly altered to hematite.

Leucoxene—The abundance of leucoxene ranges from 9.4 to 3.5 per cent of the heavy minerals. It occurs as rounded, yellowish-white grains having a porcelain appearance. Some of the grains are weakly magnetic.

Staurolite—Maximum concentration of staurolite is in the Paluxy sands in Brown, Nolan and Taylor counties. It consists of brownish-yellow, sub-angular grains with hackly fracture. A few grains have well developed concertina borders. Transparent and opaque mineral inclusions are numerous and give a porous appearance to some of the grains.

Hematite—Two types of hematite grains were encountered. Most numerous are the irregular, earthy grains with reddish-brown color in reflected light. Less common are the steel gray prismatic grains that are often arranged as rosettes (Kraus, Hunt and Ramsdell, 1936). The rosettes are concentrated in the Travis Peak formation, Wise and Parker counties, attain a maximum diameter of 2 mm., and partly enclose small grains of sand.

Garnet—About one per cent of the heavy minerals are almandite garnet. It consists chiefly of light pink, almost transparent, rounded grains that contain "spotting" surface markings. Elongated, transparent mineral inclusions with index of refraction lower than the garnets are numerous.

Quartz—Light minerals in Trinity sands other than quartz are rarely encountered. Quartz is represented by an abundance of transparent fragments with high luster and well developed conchoidal fracture and a few grains in vivid tints of red and yellow. Parallel lamellae producing "platy quartz" was noted on about 10 per cent of the grains. Inclusions consisting of opaque, irregular, black minerals, probably magnetite and volcanic dust, rounded gas bubbles, and acicular minerals, suggest that the quartz in the Trinity formation is chiefly igneous (Gilligan, 1919).

SEDIMENTS ABOVE AND BELOW THE TRINITY

The characteristics of the sediments

underlying the Trinity were secured from the deposits just below the zone of contact, whereas, materials representing complete vertical sections of the overlying, Walnut formation, were utilized. The Trinity sands grade upward into the Walnut and in the Red River area the contact is undeterminable. Though the sediments in the two formations are strikingly similar, the Walnut deposits are characterized by a finer texture, higher degree of abrasional wear especially in upper part, and the abundance of yellow oxide of iron, probably limonite.

The rocks below the Trinity range in age from early Pennsylvanian through the Permian. The distinguishing characteristics of the sediments are not applicable to the Trinity. Some of the outstanding differences include, heavy mineral assemblages, types of inclusions, and the degree of alteration. The regular inclusions (Gilligan, 1919) indicate that about 20 per cent of the quartz is metamorphic.

ENVIRONMENTS OF DEPOSITION

Trinity sediments represent two environmetal faces; offshore and marginal (Atkins, 1932). Deposits in offshore facies consist chiefly of carbonates, 80 to 90 per cent, minor quantities of fine-grained clastics, and a few well rounded grains of sand sizes. Margins of offshore facies are probably in the zone where the carbonates grade into sands and clays which to the north is Wise County and to the west Comanche County.

Conglomerates, unconsolidated gravels, sands and clays which constitute the greater part of Travis Peak and Paluxy formations represent the marginal facies of deposition. The materials of sand sizes and larger, as indicated by the high degree of abrasional wear, were subjected to extensive reworking. The coarse, basal sediments attain a thickness from 10 to 30 feet and probably represent the littoral zone in an advancing sea. The basement materials grade upward into fine pack sands and clayey materials which occupy the intermediary zone between the littoral and offshore environments.

SUMMARY

A summary of the general characteristics of the Trinity sands include: the textural range for the maximum size grade is 1/16 to 1/8 mm. to the east and 1/8 to 1/4 mm. to the west: the sand grains have undergone a high degree of abrasional wear with about 40 per cent rounded, 40 per cent sub-angular, and 20 per cent angular: the heavy minerals in order of abundance are tourmaline, ilmenite, zircon, rutile, magnetite, leucoxene, staurolite, hematite, and garnet: carbonate content of the limestones range from 82 to 89 per cent of the rock: and insoluble residues of the limestones consist of greenish-gray clay minerals, glass sherds and a few sand grains.

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JOURNAL OF SEDIMENTARY PETROLOGY, VOL. 17, NO. 2, PP. 73–76
FIGS. 1–4, AUGUST, 1947

CURRENT CRESCENTS IN THE TRIASSIC MOENKOPI FORMATION

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ABSTRACT

Crescentic structures are described from mudflat surfaces in the Lower Triassic Moenkopi formation of Arizona. These structures, through observation of recent fluvial mudflats, are demonstrated to be the crescentic impressions made by shallow water flowing around stranded pebbles and therefore of inorganic origin. They are not the tracks of animals as postulated for similar structures in the Lower Triassic Bunter formation of Germany.

The Lower Triassic Moenkopi formation of the Little Colorado River Valley contains many fluvial mudflats, the surfaces of which are generally preserved as casts by overlying lenses of sandstone or limestone. Upon some of these surfaces there occur small crescentic structures, singly or in groups. Occasionally they are associated with trackways of extinct reptiles. The crescents occur as shallow furrows in the original surfaces of the mudflats and as rounded ridges on the under surface of overlying beds. Where in groups, the crescents are oriented more or less alike; chance arrangement may give the appearance of an animal's trackway. The crescents are 3–5 cm. wide across the "horns," and while conforming usually to a semi-circle may have a box "U" shape.

Similar crescentic structures have been described in the Lower Triassic Bunter formation of Germany as the heel marks of reptiles (Willruth, Walther), and some of them seem to have been referred to a form genus and species (*Arenicoloides luniformis*) erected for "U"-shaped structures.

Investigation of recent mudflats on the San Francisco Peninsula, California, has led to what seems to be a reasonable explanation of crescentic structures of the type found in the Moenkopi formation. On deltas of certain intermittent streams, crescentic furrows were observed in association with small pieces of debris. During the last stage of flow, a thin sheet of water had eddied around stranded objects such as clay pebbles, bits of wood, willow catkins, and fruit stones so as to form shallow crescentic furrows. The horns of the crescents pointed in the direction of the current; on any one crescent the horn on the side of the strongest current was the longer. The diagrams (fig. 1) show this feature and also how the crescents are oriented with respect to small islands of very low relief—evidence that the crescents were formed during the last stages of flow.

These examples of crescents, or "current crescents," were formed by streams which declined rapidly from flood stage to a mere trickle. Deposition of a thin layer of mud on a sandy base preceded the stranding of debris which had low specific gravity and a natural buoyancy. Experiments made in the field indicate that the water must have been a thin sheet flowing at a relatively low speed, otherwise the unconsolidated mud and stranded debris would not have remained in place. Partial superposition of crescents in the Moenkopi formation (fig. 4) may have resulted from a slight shift in position of the debris while water was still flowing.

A natural corollary is that the flow of water must have ceased entirely after the crescents had been formed, so that desiccation could prepare them for preserva-

tion by subsequent sedimentation.

Among several known occurrences of current crescents in the Moenkopi formation the most remarkable is that shown in fig. 3. A rare combination of a vertebrate trackway and current crescents together with both margins of a small shallow channel are preserved here on the under side of a sandy limestone. The channel had been cut in a limey sand and was coated with a thin layer of calcareous mud which, judging from the character of the reptile trackway,[1] was apparently very sticky and slippery. However, the channel eventually became dessicated as shown by the pattern of tracks developed from the channel margins. Evidently, water had eddied around stranded pebbles of flattened clay. Subsequent deposition of the overlying stratum not only preserved the details of the mudflat surface but also the clay pebbles in position. Where the overlying stratum is broken across the center of the cast of a current crescent the clay pebble can be seen in cross-section. All current crescents observed in the Moenkopi formation seem to have been formed in this manner.

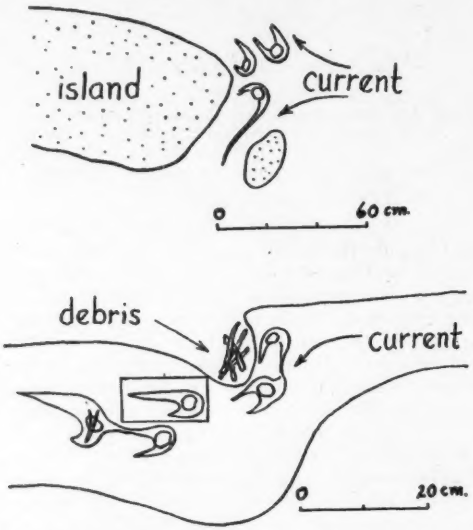

FIG. 1.—Areas of a small, dry stream channel showing where current crescents have formed around stranded debris. Areas shown have been preserved by plaster cast.

A particularly fine example of a current crescent is shown in fig. 4a as cast by the overlying sandstone. In fig. 4b its original shape as formed in a thin layer of red mud is shown by a rubber impression of the sandstone cast. The flattened pebble which caused the crescent to form has weathered from its enclosed position in the sandstone but rubber poured into the resulting cavity duplicates the pebble.

[1] *Chirotherium*, well known from the Lower Triassic of Germany, is relatively abundant in the Moenkopi formation and has been the subject of extended study by the writer. The fossil specimens described here come from the lower part of the formation in the vicinity of Meteor Crater, Arizona.

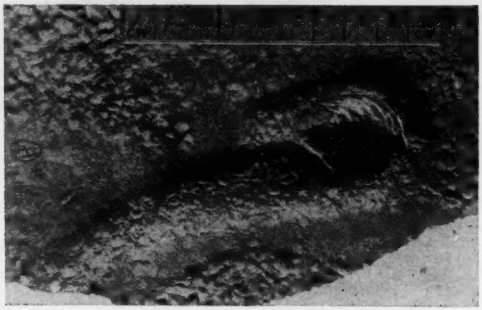

FIG. 2.—Plaster cast of current crescent caused by a stranded peach stone (original diagrammed in rectangle of fig. 1).

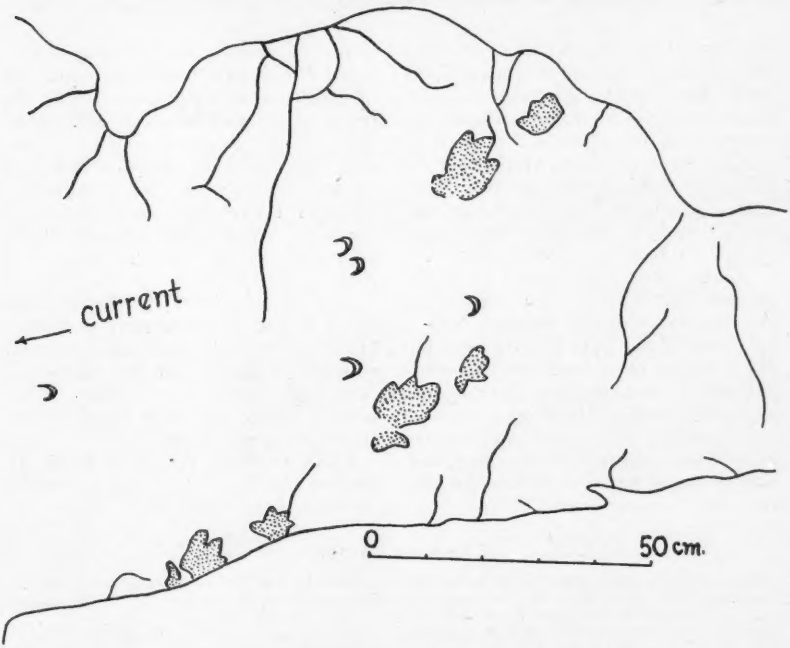

FIG. 3.—Fossil mudflat from lower Moenkopi near Meteor Crater, Arizona, showing where a large reptile (*Chirotherium*) crossed a shallow stream channel. The reptile was travelling diagonally upstream (eastward) as indicated by the current crescents. The surface shown here is only a part of an extensive area which was carefully excavated and studied.

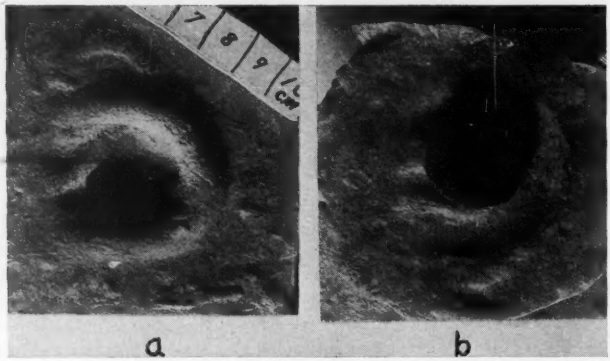

FIG. 4.—Fossil current crescent from the lower Moenkopi: a. Cast in overlying sandstone showing cavity from which original clay pebble has weathered; b. Rubber impression taken from the cast showing the original shape of the pebble and of the crescentic furrow around it.

The original was presumably of sun-baked red mud; it was flat and rounded and was 3 mm. thick and 23 mm. wide at its greatest diameter. Its origin can be reasonably explained by the common occurrence of mudflats in the Moenkopi formation. As on recent mudflats, the sun-baked mud layer apparently had become cracked and partly loosened. The next high water probably transported some of the loose mud plates downstream and a few of the smaller, lighter pieces were stranded on new mudflat surfaces. Mudflats having loose mud plates seem to have been the major course of material for numerous flat pebble conglomerates incorporated with foreset beds of Moenkopi sandstone.

Recognition of crescentic impressions in the Moenkopi formation as inorganic phenomena seems to invalidate the idea that they are footprints. Current crescents give positive indication of shallow water flowing in a definite direction, and also indicate something concerning the origin of the mudflat upon which they were formed. Regional plotting of current crescents and related evidence of stream currents in the Moenkopi formation may be a valuable adjunct to detailed study of sedimentation during Moenkopi time. Orientation of current crescents with respect to the direction of associated vertebrate trackways may afford a clue to the ecology of extinct life. For example, associated current crescents suggest that the dominant Moenkopi reptile, *Chirotherium*, habitually travelled up and down stream channels but not across them.

I wish to thank Professors Edwin D. McKee and Howel Williams for helpful criticism of the manuscript.

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FIGS. 1–2, AUGUST, 1947

MATHEMATICAL DERIVATION OF THE UNIQUE FREQUENCY CURVE

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ABSTRACT

A mathematical method of derivation of the unique frequency curve is described with illustrative examples from Trinidadian sediments; the application of the method and its limitations are briefly discussed.

INTRODUCTION

Methods of expression of mechanical analyses have not been standardized; histograms, cumulative curves and frequency curves of various types have been advocated by different workers in the field of grain size analysis. Histograms owe their popularity, despite certain obvious disadvantages (Krumbein 1934, p. 65), to their apparent ease of interpretation. They generally supply the need for frequency curves without elaborate approach. Krumbein (op. cit.) has already discussed this subject and suggested the use of the unique frequency curve which contains all the advantages of a continuous curve and is an expression of frequency distribution. The unique frequency curve is derived from the cumulative curve by graphical differentiation in which it is necessary to use a tangentometer (op. cit., p. 73). Unfortunately this is not a generally available piece of equipment and it would be convenient to possess a more universally applicable method. Krumbein (ibid. p. 67) describes the cumulative curve as the integral of its corresponding frequency curve and consequently the frequency curve is the derivative of the cumulative curve. From this statement, together with the details of the graphical method, it is obvious that there must be a mathematical device for obtaining the unique frequency curve from the cumulative curve. This paper describes the method in use in the Geological Laboratory of Trinidad Leaseholds Ltd.

ACKNOWLEDGMENTS

We wish to record our thanks to the Board of Directors of Trinidad Leaseholds Ltd., for permission to publish this information and to Dr. C. J. May (Chief Production Physicist, Trinidad Leaseholds Ltd.) who first suggested the use of Stirling's Interpolation Formula and also discussed the implications of the methods and results.

MATHEMATICAL BACKGROUND

After various trials the use of Stirling's Interpolation Formula, otherwise known as the method of "central differences," was suggested to us. This formula may be quoted as follows (Mellor 1931, p. 317):—

$$y = y_0 + \frac{x}{1}\cdot\frac{\Delta^1_0+\Delta^1_{-1}}{2} + \frac{x^2}{2!}\Delta^2_{-1} + \frac{x(x^2-1)}{3!}\times\frac{\Delta^3_{-1}+\Delta^3_{-2}}{2} + \cdots \qquad (i)$$

where (x_i, y_i) is a known series of values in which,

$$i = -n, -n+1, \cdots, -2, -1, 0, 1, 2, \cdots, n-1, n.$$

Stirling's formula supposes that the

intervals x_1-x_0, x_0-x_{-1}, $\cdots$ are unity and for our purposes these intervals in the value of "x" are equal increments, hence the formula becomes (Mellor 1931, loc. cit.):—

$$y=y_0+\frac{x}{h}\cdot\frac{\Delta^1{}_0+\Delta^1{}_{-1}}{2}+\frac{x^2}{2!h^2}\cdot\Delta^2{}_{-1}+\frac{(x+h)\times(x-h)}{3!h^3}\cdot\frac{\Delta^3{}_{-1}+\Delta^3{}_{-2}}{2}+\frac{(x+h)x^2(x-h)}{4!h^4}\Delta^4{}_{-2}+\frac{(x+2h)(x+h)x(x-h)(x-2h)}{5!h^5}\cdot\frac{\Delta^5{}_{-2}+\Delta^5{}_{-3}}{2}+\cdots. \quad \text{(ii)}$$

This represents a method of finding a value corresponding to any value of "x," lying between x_0 and x_1. From Krumbein's statement that the unique frequency curve is the derivative of the cumulative curve, this equation (ii) may be differentiated to give, instead of a value "y" at any point, the rate of change in "y" at that point. Assuming this value "y" to be very near y_0 then on differentiating "x" tends to zero and the equation becomes:—

$$(dy/dx)_{y=y_0}=1/h\left[\frac{\Delta'0+\Delta'-1}{2}-\frac{1}{6}\cdot\frac{\Delta^3{}_{-1}+\Delta^3{}_{-2}}{2}+\frac{1}{30}\cdot\frac{\Delta^5{}_{-2}+\Delta^5{}_{-3}}{2}\right]. \quad \text{(iii)}$$

This gives a value dy/dx at point y_0 for values of the equal increment in "x"—equal to "h"—and the first, third and fifth differences on either side of the value y_0.

In other words the value of the first differential at any point (x_0, y_0) is equal to:—

$\frac{1}{2}h$ (the sum of the first differences on either side of the central value (x_0, y_0) $-\frac{1}{6}\times$the sum of the third differences on either side of the central value etc., etc.), where the equal increment in "x" is "h."

The number of terms to which it is necessary to proceed depends entirely on the accuracy required. In practice it will be found unnecessary to proceed beyond third differences. It can readily be seen that the terms decrease very rapidly both because of smaller coefficients and diminishing differences.

APPLICATION TO SPECIFIC EXAMPLES

In order to apply the method to grain size analyses it is most convenient to construct the cumulative curve on arithmetic paper; the use of Krumbein's phi scale (Krumbein and Pettijohn 1938, p. 80) considerably facilitates such work, and Keuffel and Esser No. 334-2TN is a suitable graph paper.

The intervals of the equal increment (h) are then determined upon; $\frac{1}{4}\phi$ or $\frac{1}{8}\phi$ have been most generally used during our work in Trinidad. The cumulative "y" figures are read off the curves at equal intervals of "x" and are tabulated as in table 1, columns 1 and 2 (see also figure 1, curve 1). Columns 3, 4, and 5 contain the first, second and third differences respectively. The third differences are summed in column 6 and multiplied by minus $\frac{1}{8}$ to give column 7. Column 8 consists of the summed first differences and columns 7 and 8 are added algebraically to obtain column 9. Finally these figures are multiplied by the factor $\frac{1}{2}h$ to give the unique frequency figures in column 10. The factor $\frac{1}{2}h$ is equivalent to multiplying by 2 when $h=\frac{1}{4}\phi$ and by 4 when $h=\frac{1}{8}\phi$.

The unique frequency figures may now be plotted either on the original graph for studying its relation to the cumulative curve or on a separate sheet for comparison with other frequency curves. It is a good general plan to choose typical examples of cumulative curves from the set being studied and to plot one unique frequency curve as a type curve for each group of similar cumulative curves.

It will be noted that during the computations for the unique frequency figures the first and last two values of "y" are lost. If it becomes necessary to obtain these figures to complete the frequency curve—and for well-sorted sands this is generally the case—readings of "y" over smaller intervals of "x" may be taken

covering the ends of the cumulative curves; similarly for emphasis of modes or inflection points more detail may be obtained by increasing the number of readings or decreasing the interval of "h" over selected parts of the cumulative curve. In carrying out the tabular computations use of printed ¼-inch squared paper will be found to facilitate the work.

TABLE 1. *Mathematical Derivation of the Unique Frequency Curve of a Miocene Sand from Trinidad*
(See figure 1, curve 1)
$h = \frac{1}{4}\phi$; origin $= 2.50\phi$

1	2	3	4	5	6	7	8	9	10
x	y	$\Delta 1$	$\Delta 2$	$\Delta 3$	$\Sigma\Delta 3$	$\times -\frac{1}{6}$	$\Sigma\Delta 1$	$7+8$	$\times \frac{1}{2}h$
2.50[1]	0.50								
		0.50							
2.75	1.00		0.50						
		1.00		1.50					
3.00	3.00		2.00		0.50	−0.08	4.00	3.92	7.84
		3.00		− 1.00					
3.25	5.00		1.00		11.00	−1.83	7.00	5.17	10.34
		4.00		12.00					
3.50	9.00		13.00		24.00	−4.00	21.00	17.00	34.00
		17.00		12.00					
3.75	26.00		25.00		−48.00	8.00	59.00	67.00	134.00
		42.00		−60.00					
4.00	68.00		−35.00		−30.00	5.00	49.00	54.00	108.00
		7.00		30.00					
4.25	75.00		− 5.00		34.50	−5.75	9.00	3.25	6.50
		2.00		4.50					
4.50	77.00		− 0.50		5.50	−0.91	3.50	2.59	5.18
		1.50		1.00					
4.75	78.50		0.50		0.00	0	3.50	3.50	7.00
		2.00		− 1.00					
5.00	80.50		− 0.50		0.00	0	3.50	3.50	7.00
		1.50		1.00					
5.25	82.00		− 0.50		1.50	−0.25	2.50	2.25	4.50
		1.00		0.50					
5.50	83.00		0.00		1.00	−0.01	2.00	1.99	3.98
		1.00		0.50					
5.75	84.00		0.50		− 0.50	0.08	2.50	2.58	5.16
		1.50		− 1.00					
6.00	85.50		− 0.50						
		1.00							
6.25	86.50								

[1] U. S. Standard Sieves, W. S. Tyler Co., Cleveland, Ohio.

LIMITATIONS OF THE METHOD

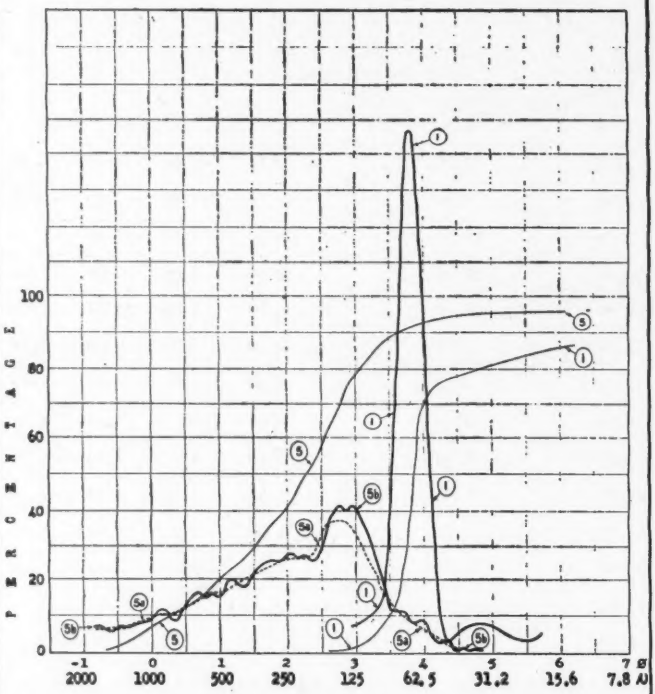
Inaccuracies in the method due to smoothing of the cumulative curve have been emphasized by Krumbein (Krumbein 1934) and the tendency for the unique frequency curve to exceed 100% in cases of very steep cumulative curves —well-sorted sediments—has been attributed (ibid.) to the fact that the unique frequency curve is a measure of the change of slope of the cumulative curve. In addition, in the mathematical method of derivation herein described, when the sediment is extremely well-sorted and unimodal, there is often a tendency for the development of negative values around minima on the frequency curve; these are presumably the result of inaccuracy in the readings from the very steep cumulative curve. They

T. L. L. G. P. & S. DIV.

Fig. No. 1
Rep. No.
Drg No. 1566x

CUMULATIVE AND UNIQUE FREQUENCY CURVES OF SOME TRINIDAD SEDIMENTS.

By J. C. Griffiths.



(1) Cumulative and Unique Frequency Curve of Middle Miocene Sand, South Trinidad.

(5) Cumulative Curve of Oligocene Sand, South Trinidad.

(5a) Unique Frequency Curve of Oligocene Sand, South Trinidad; ¼ ø interval, to 3rd differences.

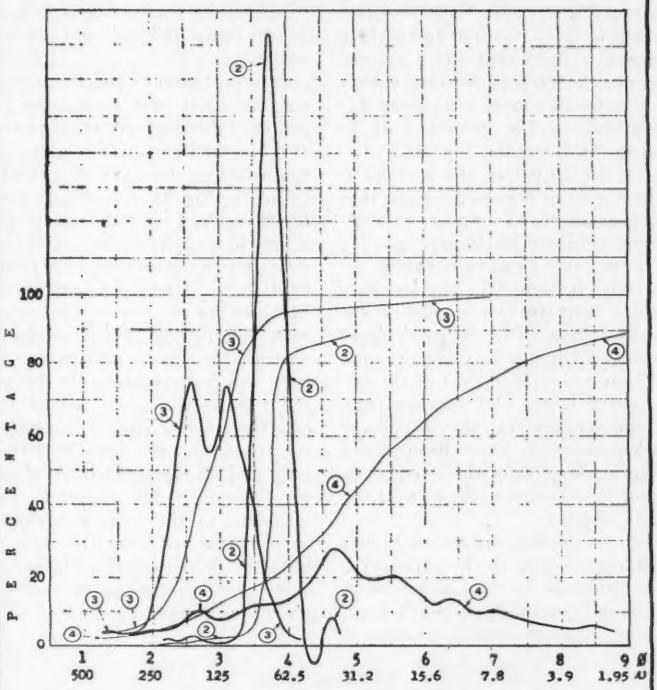
(5b) Unique Frequency Curve of Oligocene Sand, South Trinidad; ⅛ ø interval, to 5th differences.

T. L. L. G. P. & S. DIV.

Fig. No. 2
Rep. No.
Drg. No. 1566x

CUMULATIVE AND UNIQUE FREQUENCY CURVES OF SOME TRINIDAD SEDIMENTS.

By J. C. Griffiths



② Middle Miocene Sand, South Trinidad; Unimodal curve with negative minimum.

③ Middle Miocene Sand, South Trinidad; Bimodal curve.

④ Upper (?) Miocene Laminated Sand, South Trinidad; Polymodal curve in silt grade.

do not occur in the graphical method described by Krumbein.

In many sediments in Trinidad these curious aberrations are common and considerable (see figure 2, curves 2 and 4) and to offset these tendencies a very close sieve interval is adopted over the range between 250 and 62.5 microns as follows —250, 210, 177, 149, 125, 105, 88, 74, and 62.5 microns.[1] This covers the range in which the bulk of the material in many samples occurs. In addition, of course, the silt and clay fractions are determined by pipette sedimentation (Rittenhouse 1939, p. 88) at intervals of 1ϕ between 62.5 microns and 1 micron. This reduces the errors due to inaccuracy in the cumulative curve, principally due to smoothing in the steeper part as pointed out by Krumbein (op. cit.).

Another limitation in the method is also noteworthy; it may be imagined that by using smaller and smaller intervals (h) greater accuracy in the expression of the frequency curve can be obtained but such practice is limited by the accuracy with which ordinates can be read off the cumulative curve. This is particularly clearly seen in figure 1, curve 5*b*, and figure 2, curve 4, in that part of the frequency curve below 31.2 microns (4ϕ), where fluctuations in the frequency curve are presumably due to inaccuracies in *a*) the readings from the cumulative curve and *b*) the original drawing of the cumulative curve.

It will be readily understood that slight change of slope in the cumulative curve is sufficient to turn a unimodal curve into a bimodal type. Small inaccuracies in the analysis or of readings of "y" readily lead to this. In our experience however, the converse is the more dangerous, i.e., either screen intervals too far apart or too generous smoothing of the cumulative curve leads to all curves being unimodal. Such errors on either side are inherent in both mathematical and graphical methods of derivation of the unique frequency curve. Closer interval for screening, greater care during drawing of the cumulative curve together with repeated analyses of a large number of samples, or in other words experience of the investigator, appears to be the only method of reducing such errors.

Interpretation of the frequency curve resolves itself into comparisons of the degree of development of different modes and here another error must be guarded against. This difficulty suggested to the author by Dr. May, is due to the use of the phi scale. Thus although the phi scale is used as an arithmetic scale it is related directly to a logarithmic base (Krumbein 1934, and Krumbein and Pettijohn 1938) and in the case of a bimodal curve with equally developed modes in for example the central part of the intervals $1–2\phi$ and $2–3\phi$ respectively the mode in the $1–2\phi$ interval is in actual fact the principal mode. This is because during the transformation from logarithmic to arithmetic phi scale the interval $2–3\phi$ has been relatively less reduced compared with that of the $1–2\phi$ interval. Fortunately such ambiguity is not usually sufficient to cause any ambiguity in the qualitative comparison of modes of the average sediment.

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CLEANING MINERAL GRAINS FOR PETROGRAPHIC STUDY

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ABSTRACT

To clean or disaggregate mineral grains prior to microscopic examination, phosphoric acid, tartaric acid, and citric acid are satisfactory and may be particularly useful in certain problems.

Before microscopic examination, sedimentary petrographers commonly boil detrital grains in dilute hydrochloric acid (HCl) to dissolve carbonates and iron oxides which may make the grains cloudy and difficult to identify. This treatment also dissolves apatite and attacks some silicates. The use of hydrochloric acid for this purpose, and also the use of a number of other inorganic acids and acid salts, is mentioned in all standard texts on sedimentary petrography.

Other acids that can be used for the clarification of detrital grains are phosphoric acid (H_3PO_4) and the organic acids—citric ($C_6H_8O_7$), tartaric ($H_2C_4H_4O_6$), and oxalic ($H_2C_2O_4$). All these acids dissolve carbonates. As solvents for iron the three organic acids are effective because they form stable complex ions with iron. Phosphoric acid also dissolves iron oxides very readily. Indeed, both phosphoric acid and oxalic acid are used commercially in some rust removers.

Mention of these acids in the geologic literature is scarce or lacking. Holmes states that the use of citric and acetic acids has been recommended for removing carbonates without affecting silicates. Among recommendations for the use of various inorganic acids, Grout states: "To remove calcite from an altered rock use acetic acid"; but he does not mention other organic acids. Soil science literature, on the other hand, describes a number of applications of oxalic and tartaric acids or oxalates and tartrates for the removal of iron oxides from soils and clays preparatory to chemical, x-ray, and petrographic analysis and also for the determination of free iron oxides in the soil. The most recent paper on this subject is by Dion; it contains a summary of previous use of these acids by soil scientists and cites appropriate references. Dr. I. Barshad[1] of the Division of Soils, University of California, has used dilute citric acid to clean iron oxides from the sand and silt particles in soils. In general, the problem of sample preparation is more complex for the soil scientist than for the sedimentary petrographer, and many of the techniques used by soil scientists are more exact and complicated than would be favored by most petrographers except for special problems.

Listed in the order of increasing strength, the acids investigated[2] by the author are citric, tartaric, oxalic, and phosphoric. Simply by boiling detrital grains in dilute solutions of these acids iron oxide coatings can be removed. Each of the acids also dissolves calcite and dolomite and attacks apatite, but none has any noticeable effect on silicates normally present in sediments. The following is a brief statement of the qualitative effects of each acid.

Phosphoric acid. Syrupy phosphoric acid (H_3PO_4, 85%) diluted to about 20%

[1] Personal communication.

[2] Acetic acid was also considered because mention of it appears in the literature. Its action on calcite was too slow to make further investigation desirable. It does not form a complexion with iron and has little effect on iron oxides.

is a very effective solvent for iron oxides and will remove them from sand by boiling for as little as 5 to 10 minutes; indeed, the iron oxides are removed from some sands before the acid reaches the boiling point. The solution remains colorless during this treatment, and the treated grains are as clean as or cleaner than when digested in hydrochloric acid. Dilute phosphoric acid also leaches a little iron from fresh biotite, as shown by the very slightly lighter color of the biotite after digestion, but it will not leach all the iron in biotite as does hydrochloric acid.

Calcite dissolves rapidly in warm 20% phosphoric acid, but the rate at which it dissolves depends largely on the size of the calcite grains and the temperature of the acid. Apatite also dissolves when boiled in phosphoric acid, but much less rapidly than in hydrochloric acid. For example, one gram of apatite crushed between ¼ and 1 millimeter dissolved in 50 cc. of 20% phosphoric acid after boiling for 30 minutes; whereas the same amount of the crushed apatite dissolved completely after boiling for only 5 minutes in 20% hydrochloric acid. A weaker solution of phosphoric acid dissolves apatite still more slowly.

Oxalic acid. By boiling detrital grains in a solution of oxalic acid (approximately 9 grams of acid per 100 grams of water) iron oxides are removed very rapidly and just as completely as by boiling in hydrochloric acid. Part of the iron is leached from fresh biotite as shown by the yellow color of the solution when pure biotite is treated.

The action of oxalic acid on calcite, dolomite, and apatite is not strictly comparable with that of the other acids investigated. These minerals are destroyed but a new colorless crystalline material having a faint green pleochroism and strong birefringence is formed, presumably the very slightly soluble calcium oxalate (whewelite). For example, crushed calcite boiled in oxalic acid was replaced by a microcrystalline aggregate of the calcium oxalate. This effect will undoubtedly limit the use of oxalic acid in petrography, although it is very efficient solvent for iron oxides.

Tartaric acid. A solution of tartaric acid (20% by weight) readily dissolves iron oxides in sands, and its effect on biotite is negligible. Grains boiled in this solution are practically as clean as those treated with hydrochloric acid. Hot tartaric acid dissolves calcite at a moderate rate and dolomite more slowly; but the rate depends on the grain size of the carbonates, and a larger volume of acid is necessary than with the stronger acids. Apatite is slowly dissolved; one gram of it crushed between ¼ and 1 millimeter showed a weight loss of 25% after boiling for 2 hours in 20% tartaric acid. Nevertheless, it is likely that small quantities of finer grained apatite would be completely dissolved by such prolonged treatment. The possible use of tartaric acid in the treatment of sediments is illustrated by its action on several very fine grained sandstones so cemented by calcium carbonate as to require chemical disaggregation. These were completely broken down within 30 minutes by boiling in dilute tartaric acid, and the remaining heavy minerals were found to contain very abundant apatite as slightly rounded grains.

Citric acid. A solution of this acid (20% by weight) reacts in every way like tartaric acid but, being weaker, is slower in its action. However, detrital grains boiled in it for a few minutes can be nicely cleaned, and it is possible to dissolve the calcite cement from fine grained sandstones without dissolving more than a negligible amount of the apatite present.

Since investigating the effects of these various acids on sands, citric acid has been used to clean several samples of crushed iron-stained granite before study of the accessory minerals present. Both the iron oxide stains, and the iron dust from the mortar used in crushing, were completely removed by boiling in dilute citric acid for 10 minutes, and the loss of apatite is thought to have been

negligible. Apatite among the heavy accessory minerals shows easily recognizable crystal forms, and if the crystals are rounded by solution in the acid the effect is scarcely noticeable. Certainly the percentage of apatite by number of grains has not been altered even if there has been some loss of apatite by weight.

CONCLUSIONS

Digestion in 20% phosphoric acid is an effective method of cleaning detrital grains and of disaggregating sandstones cemented by calcium carbonate. Apatite will generally be dissolved by the treatment necessary for disaggregation, but the silicates are not noticeably attacked. It might be used instead of hydrochloric acid except when it is desirable to leach the biotite completely (baueritization).

Both tartaric and citric acid are to be recommended and should be tried as cleaning and disaggregating agents in studies requiring a minimum attack of the solvent on apatite and other minerals.

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A MERCURY VALVE FOR SEPARATING HEAVY MINERALS BY THOULET OR SONSTADT SOLUTION (K_2HgI_4)

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The corrosive action of Thoulet or Sonstadt solution (specific gravity 3.18) on organic matter and the decomposition it undergoes on coming in contact with metals, prohibits the use of rubber tubing and metal clamps. A separating funnel with glass stopper is often used but this at times fails to serve the purpose satisfactorily because of the clogging up of the passage in the stop-cock by the sinking material. While studying the heavy minerals of soils, the following contraption (Text-fig. 1) was devised to overcomes the difficulty of clogging up.

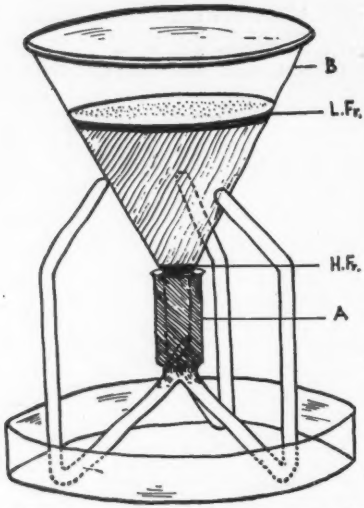

FIG. 1.—Mercury valve for separating heavy minerals. (A) Mercury tube, (B) Funnel covered with a watch glass, (H. Fr.) Heavier fraction, (L. Fr.) Lighter fraction.

B is an ordinary funnel with a short stem dipping in a small tube A full of mercury. The tube A is kept in the upright position by three vertical glass supports fused to the bottom of the tube A. The whole unit is placed in a petri dish of convenient size. Mercury in A because of its high specific gravity (sp. gr. = 13.6) is able to support a sufficiently long column of Thoulet solution (sp. gr. = 3.18). In fact any length may be supported by regulating the length of the stem of the funnel and the depth of the tube A. The contact of mercury with K_2HgI_4 prevents its decomposition.

A convenient quantity of Thoulet solution is placed in the funnel and the powder to be analyzed is added to it. Stirring is done by means of a glass rod. The heavier grains sink to the surface of mercury inside the funnel. Raising the funnel slowly reduces the effective height of the mercury column and a part of the solution along with the heavy mineral residue (H. Fr.) flows out into the petri dish placed below. The funnel is again lowered and the flow stops. The petri dish is replaced by another one by lifting the unit by one of the vertical supports. Any mercury that might overflow is transferred back. A green deposit appears on the surface of the mercury in the tube if washing is done by water alone, but a few drops of dilute KI solution help to restore the shining surface of the mercury.

It is hoped that this device will prove helpful in the study of heavy minerals

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CONTRIBUTIONS TO THE JOURNAL OF SEDIMENTARY PETROLOGY

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A casual checking of the sources of articles contributed to the *Journal of Sedimentary Petrology* revealed a number of interesting relationships. When

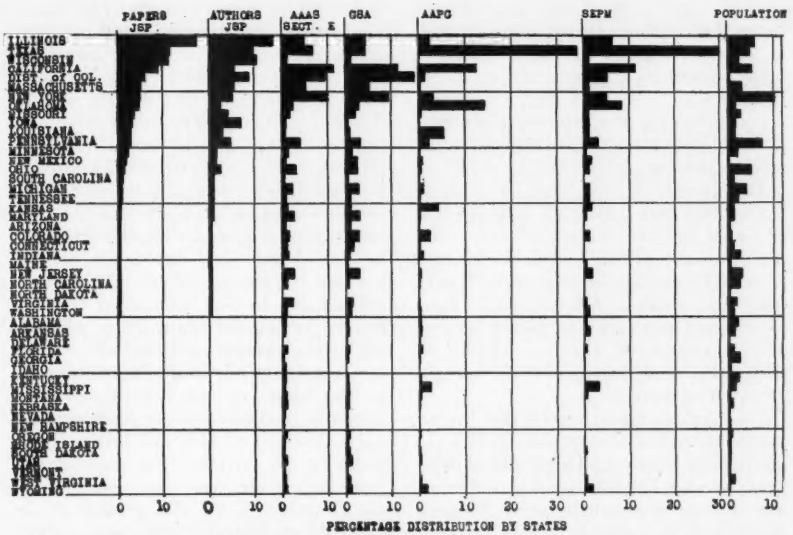

FIG. 1.—Bar graphs showing the percentage distribution by states of articles contributed to the *Journal of Sedimentary Petrology*. The percentage distribution by states of the members of geological organizations who are living in continental United States is added for comparison.

Papers JSP—distribution by states of the 204 papers contributed to *Journal of Sedimentary Petrology* during the first sixteen years of publication—to Dec. 31, 1946.

Authors JSP—distribution by states of the 169 authors who contributed papers to the *Journal of Sedimentary Petrology* during the first sixteen years of publication.

AAAS, SECT. E—distribution by states of the 1321 members of American Association for Advancement of Science, Section E, Geology and Geography in August 1946 (personal communication, AAAS secretary's office).

GSA—distribution by states of the 798 members of Geological Society of America in June 1946 (*Proc. Geol. Soc. Am., Ann. Rept. for 1945*, pp. 161–187).

AAPG—distribution by states of the 4270 members of American Association of Petroleum Geologists in March 1946 (*Bull. Amer. Assoc. Petrol. Geol.*, vol. 30, pp. 439–454, *1946*).

SEPM—distribution by states of the 157 members of Society of Economic Paleontologists and Mineralogists in January 1947 who subscribe to *Journal of Sedimentary Petrology* (personal communication, SEPM business manager).

Population—distribution by states of total population according to 1940 census.

some of the outstanding points were investigated further a small compilation of statistics accumulated. Because some of the relationships may be of interest to sedimentationists they are presented herewith.

The analysis is based on the author and the address given below the title of all articles published in the *Journal* during the first sixteen years of it publication—from Jan. 1, 1931 to Dec. 31, 1946. Far-reaching conclusions should not be attempted because the *Journal* contains only part of the contributions to sedimentation during this period, many other articles having appeared in other periodicals and were not included. Also, it was recognized that, at least in some instances, the address given was not the same as that at which the work was done.

During the sixteen years, a total of 228 articles were published, 10.5 per cent of which were from foreign sources. Of the remainder, all written within the continental United States, 84.9 per cent were from universities, 8.3 per cent from federal and state surveys and museums, 3.9 per cent from industry, chiefly oil companies, and 2.9 per cent from unaffiliated authors.

The articles from within the United States were tabulated by states, as summarized in figure 1. These 204 articles were written by 169 persons, either as sole authors or as collaborators. Because this sample is relatively small, the contributions by a few prolific authors give some states unduly high representation. Eight authors contributed four to twelve articles; thus, 4.7 per cent of the authors wrote 27.4 per cent of the articles. In spite of this weighting, it is believed that the tabulation of figure 1 has some validity as a rough general indication of the areas of most active sediment research. For purposes of comparison, the membership arranged by states for several large geological associations are included. It should be noted that the membership lists are for the last year of the sixteen year period studied.

The figure shows that 49.7 per cent of the articles were contributed by four states: Illinois, Texas, Wisconsin, and California. Two of these states are major oil producing areas, as indicated also by AAPG enrollment. The other two states have active faculties in sedimentation at the universities. The District of Columbia is a prominent contributor because of the concentration of federal surveys and museums; the figure for the district would be even higher had not a few articles written by survey members been addressed at branch offices in various states. Among the states from which a few articles were contributed are most of the remaining oil producing states. No articles whatever were contributed from 19 states, conspicuous among which are the southeastern states and those western states having relatively low populations. None of the non-contributing states are well represented in the geological association membership rolls, and mostly to a degree even less than in proportion to total population.

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